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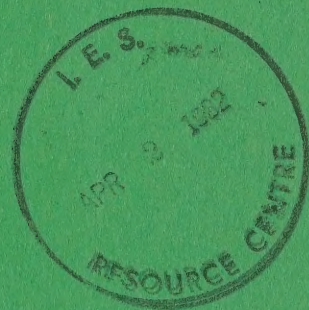


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RESEACH REPORT No. 82

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Gérard J. M. Raymond
Deputy Minister

MONITORING OF SELECTED TRACE ORGANICS
DURING BIOLOGICAL WASTEWATER TREATMENT

RESEARCH REPORT # 82

BY

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THE ONTARIO MINISTRY OF ENVIRONMENT

&

ENVIRONMENTAL PROTECTION SERVICE

FEBRUARY 1982



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ACKNOWLEDGEMENTS

Financial support for this project was provided jointly by Environment Canada, Environmental Protection Service (EPS) and the Ontario Ministry of Environment (MOE).

Appreciation is expressed to the scientific liaison officers, Mr. George Zukovs of MOE and Mr. Trevor Bridle of EPS.

The excellent analytical support provided by the MOE, OTC laboratory under the supervision of Mr. Ron Bonner and Ms. G. Foster and the Analytical Services Section, Inland Waters Directorate, Ontario Region at Burlington under the supervision of Mr. John Coburn is gratefully acknowledged.

ABSTRACT

This study was the first effort in Ontario to monitor the fate of trace organics contaminants in passage through a conventional activated sludge plant.

In the first study phase a field sampling program was carried out in a full scale WPCP which receives about 26% by volume of its raw sewage from a single organics manufacturing plant. All WPCP samples were extracted and an organics scan by GC/MS was performed on all extracts. Benzothiazole, diethyl phthalate, dioctyl phthalate, diphenylamine, 2-methyl-mercapto benzothiazole and analine were the major organic contaminants detected in all the influent, effluent and sludge samples.

In a subsequent study phase an attempt was made to determine the fate of these six contaminants in passage through two pilot scale activated sludge reactors and a pilot scale anaerobic digester. Due to poor accuracy in quantitative measurement, it was impossible to perform mass balances for the six compounds around the three reactors. Nonetheless, results strongly indicated that analine removal occurred during activated sludge treatment, and dioctyl phthalate accumulated in the activated sludge solids.

It was recommended that if quantitative results are needed in future studies, a more extensive effort should be devoted to extraction/analytical methods development.

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NOMENCLATURE

DO	dissolved oxygen
EPA	Environmental Protection Agency
EPS	Environmental Protection Service
GPC	gel permeation column
HRT	hydraulic retention time
MLSS	mixed liquor suspended solids
MOE	Ontario Ministry of the Environment
POTW	public owned treatment works
SRT	sludge retention time
SWD	side water depth
TOC	total organic carbon
WPCP	water pollution control plant

STUDY SUMMARY

1.0 Literature Review

1.1 Seven different extraction procedures for trace organics analysis were reviewed. It was found that none of these methods can be universally applied to analyse various quality sewage influent, effluent, and sludge samples.

1.2 Most large scale trace organics monitoring programs on specific industrial and/or municipal sewages, e.g. the US EPA 40 plants study are still on-going. As a result, very little data on the treatability of trace organics in sewage treatment plants are available. In general there are three major removal mechanisms for trace organics. Certain volatile and non-polar organics can be removed by air-stripping during activated sludge treatment. Some compounds tend to concentrate in the sludge streams and can therefore, be removed by solid-liquid separation. Many compounds can be removed by biodegradation either readily or after a period of acclimation.

1.3 Chlorine can reduce the concentrations of certain organics in the treatment plant effluents through oxidation reactions. On the other hand, substitution reactions can lead to the formation of new chlorinated organic compounds.

2.0 Phase 1 - Study Results

2.1 The entire study (Phases 1 and 2) was carried out at a Central Ontario secondary WPCP which receives a significant portion of its raw sewage from a nearby chemical manufacturing plant. In Phase 1, raw sewage, final effluents (before and after chlorination), primary and waste activated sludges were sampled from the "full-scale" WPCP and were analysed by GC/MS, on two separate occasions. On both occasions, benzothiazole, diethyl phthalate, dioctyl phthalate, diphenylamine and 2-methylmercapto benzothiazole were noted to be the major organic contaminants in all the samples analysed. A few other organic compounds were also noted to present at significant concentrations in some of the samples analysed.

3.0 Phase 2 - Study Results

3.1 The five major organic contaminants noted in Phase 1 samples (benzothiazole, diethyl phthalate, dioctyl phthalate, diphenylamine, and 2-methylmercapto benzothiazole) plus aniline were closely monitored in the influent, effluent and waste activated sludge samples collected from two bench scale nitrification reactors. These six compounds were also monitored in the feed and the effluent streams of a bench scale anaerobic sludge digester. Off-gas from the three bench scale reactors were also sampled and analysed. All samples collected were separated by filtration into liquid and solid fractions. The liquid fractions were extracted by the standard EPA "base/neutral

liquid-liquid extraction" protocol using methylene dichloride as organic solvent. The solid fractions were extracted with methylene dichloride, assisted by ultrasonic disruption. The extracts were then analysed by GC/MS.

- 3.2 The reproducibility, and recovery efficiency for the six selected organic compounds by the aforementioned methods were found to be extremely poor and erratic when examined in duplicate and spiked samples, respectively. Inappropriate extraction procedures were suspected to be the major source of error. Other factors such as: compounds occurring at concentrations close to or below the GC/MS quantification limit, volatilization, and relatively low solvent recoveries could also have contributed to the overall analytical errors.
- 3.3 As a consequence of poor reproducibility and recovery efficiency, aniline was the only compound showing strong evidence of being removed during nitrification treatment. Dioctyl phthalate was observed to be strongly hydrophobic, and therefore, its removal in the liquid effluent stream is expected through solids settling.
- 3.4 No trace organic contaminants were detected in the off-gas samples collected above the two bench scale nitrification reactors. It is suspected that the sampling method (Tenax organic traps) used is an inappropriate means for gas sample collection.

- 3.5 Aniline, benzothiazole and diphenylamine in the feed and in the effluent streams of the bench scale anaerobic sludge digester were noted to occur at concentrations below the GC/MS "minimum quantification limit". Diethyl phthalate, dioctylphthalate, and 2-methylmercapto benzothiazole occurred at levels significantly higher than the GC/MS "minimum quantification limit" in both the feed and effluent streams of the sludge digester.
- 3.6 The sludge digester gas was found to contain measurable quantities of several organics including methane, n-propyl benzene, cyclohexane, toluene, cumene, chloroform, m-xylene, carbon disulphide, trichloroethylene, and tetrachlorethylene and propane.

RECOMMENDATIONS

1. Prior to carrying out any further organics monitoring program, considerable effort should be devoted to developing or refining appropriate extraction methodologies suitable for different quality/types of samples. The methodologies must be statistically assessed/compared by a reliable "quality assurance/quality control" program. The precision and accuracy data established for each comparative method must be properly documented for future reference.
2. To minimize the overall costs for any future organics monitoring program, a "short list" of organic compounds must be developed and prioritized according to; specific environmental concern/significance, and the usefulness as a "surrogate" parameter for assessing effluent quality/health risks. The EPA Priority Pollutant List, the Great Lakes Water Quality Agreement Toxic Compounds List, etc, can be used as a starting basis for developing such a "short-list".
3. Specific mass balance studies with a bench scale activated sludge treatment system should be carried out at ambient and augmented (spiked) trace organic levels, such that the relationships between organics removal (by biodegradation and/or air stripping) and process operating conditions can be developed.
4. In order to develop a reference data base for trace organic levels in Ontario municipal wastewaters and sludges, it is recommended that a sampling program be carried out at several (at least 20) wastewater treatment facilities. These

facilities should encompass a variety of treatment processes, e.g. lagoons, primary, conventional activated sludge, and advanced treatment processes. The study should also consider municipalities with varying degrees and types of industrial contribution. Composite samples should be collected from each facility influent, effluent, and sludge streams at least quarterly for a one year period.

1.0 Background, Objectives And Scope

1.1 Background

In response to the concern on possible dissemination of hazardous organic pollutants into the environment through sewage effluent/sludge discharges, the Ontario Ministry of the Environment (MOE) and the Environmental Protection Service (EPS) of Environment Canada jointly initiated the study reported herein.

The original goal of the study was to assess the ability of conventional sewage treatment technology to remove hazardous organic pollutants. This goal was to be achieved by means of quantitatively tracing the fate of a selected number of organic pollutants as they passed through two bench-scale nitrification reactors and an anaerobic sludge digester. However, due to a tremendous amount of analytical difficulties encountered during the study, and limited resources, it became apparant that such a goal could not be properly fulfilled. Consequently, the study objectives were revised as outlined below.

1.2 Objectives

Three revised study objectives were:

- (1) To conduct a literature review of extraction procedures available for the analysis of trace organic pollutants in municipal WPCP sludges;
- (2) To conduct a literature review on the treatability of organic pollutants by sewage treatment processes;
- (3) To conduct a preliminary examination on the adequacy/problems associated with the current US EPA "Liquid-Liquid Extraction/Analytical Protocol" when applied to quantitatively measure a selected number of organic pollutants in municipal WPCP final effluent and digested sludge samples.

1.3 Scope

The study was divided into two phases. In Phase 1 a preliminary GC/MS screening program was carried out at a full scale municipal secondary WPCP. The purpose of this phase was to identify major trace organic contaminants occurring in the subject WPCP raw sewage, final effluent and sludge samples, such that a short list of hazardous organic contaminants could be prepared for Phase 2 monitoring.

In Phase 2 the selected number of trace organic contaminants were monitored in the sewage influent, effluent and sludge samples collected from two bench-scale nitrification reactors, and one bench-scale anaerobic sludge digester. These bench-scale reactors were being operated on-site at the subject WPCP. Their operation conditions such as hydraulic retention time (HRT), sludge retention time (SRT), etc, were carefully controlled, and documented. The preliminary evaluation on the adequacy/problem associated with the US EPA "Liquid-Liquid Extraction/Analytical Protocol" was carried out by means of measuring the selected organic contaminants in duplicate samples, and in spiked samples.

An extensive literature review on the existing extraction methodologies for the analysis of organic contaminants in sludge samples, and the treatability of the selected organic contaminants by conventional treatment technology was also carried out in Phases 1 and 2, respectively.

The entire study was carried out at a municipal secondary WPCP located in Central Ontario. The WPCP receives a significant portion of its raw sewage from a nearby organic chemical manufacturing plant, and detectable levels of organic contaminants had previously been measured in the WPCP effluent. Furthermore, detailed treatability studies were being conducted on-site with bench-scale reactors. Consequently, the subject WPCP was selected for the above reasons.

2.0 Literature Review

2.1 Review Of Extraction Methodologies

Highly volatile organics are usually amenable for extraction by a purge and trap method (e.g. EPA, 1979), hence, only those procedures pertaining to the extraction of semi-volatile organics were reviewed. Several extraction methodologies reviewed were further discussed with organic analytical chemists at the CCIW (Coburn, 1979), MOE (Foster, 1979) and EPA (Cater, 1979). In addition, information compiled by the EPS and MOE technical staff during a site visit to EPA analytical laboratories (July, 1980) were also incorporated in this review.

It is noted during the review that few organic extraction procedures have been developed specifically for wastewaters with relatively high solids content (i.e. > 30-mg/L) and sludges. Furthermore, there is no published data comparing the relative accuracy and precision of the currently available sludge extraction procedures. Only recently, the EPA in the United States and the EPS in Canada have initiated projects designed to gather such data, and to develop new and more precise extraction methodologies. In general, extraction techniques for semi-volatile organics fit into one of the categories summarized in Table 1. This Table gives a brief description of the procedures involved in each method, and its overall advantages and disadvantages. In regard to the existing published extraction procedures the following generalization can be made:

- (1) No extraction procedure can be universally applied to all wastewater and sludge samples;

TABLE 1
SUMMARY OF AVAILABLE EXTRACTION METHODOLOGIES

METHOD	REFERENCE(S)	BRIEF DESCRIPTION	DISADVANTAGES	ADVANTAGES
Conventional Separatory Funnel	EPA (1977) EPA (1979a)	Extract sample with several aliquots of a general solvent, usually methylene chloride, in separatory funnel. Allow layers to separate and drain solvent layer. Mechanical means and excess solvent are commonly employed in attempts to break emulsions. Removal of excess water by filtration through anhydrous Na_2SO_4 . Clean up and roto vap to final extract volume.	Emulsions are usually formed when solids contents are relatively high resulting in high solvent losses. Not suitable for sludges.	Minimum equipment requirements. Simple methodology most appropriate for water samples with low suspended solids content.
Continuous Extraction	EPA (1977)	Extract for 24 hours in a continuous extraction apparatus (various types available, e.g., Soxhlet). After extraction solvent is subjected to similar clean up and concentration procedures as above.	Not suitable for sludges unless samples have been homogenized to break up solids. Specialized equipment requirement. Potential for losing some of the more volatile organics during higher temperature extraction.	Higher solvent recoveries for sludges than separatory funnel method.
Steam Distillation	Veith and Kiwus (1977)	Sample (after homogenization, if desired) is adjusted to required pH and placed in distilling flask fitted with a modified Nielson-Kryger condenser. The solution is boiled (1-7 hours) and the steam distillate condenses on the inside wall of the cooling jacket. The condensate passes through a layer of lower density solvent (i.e., benzene or isooctane) into which the organics are partitioned. Water passes through into an overflow tube and serves as a solvent trap. The extract is removed through a stopcock and generally does not require any further clean up other than filtration through Na_2SO_4 .	Sludges samples should be homogenized prior to distillation. Potential for losing some organics on boiling.	Simple procedure. No extract clean-up required.
Sediment Extraction Procedures (Homogenization/Filtration)	EPA (1979a) Coburn (1979)	Air dry sediment sample at ambient temperature. Weigh portion of partially dried sediment into stainless steel beaker. Add solvent to the dried sediment and homogenize with an ultrasonic probe. Filter homogenized sample and wash filter cake with solvent. Clean up and concentrate extract as in separatory funnel method.	More labor and equipment intensive than previous methods.	Suitable as general extraction method for sludges.
Sludge/Sediment Method (Homogenization/Centrifugation)	Midwest Research Institute (1979)	Transfer aliquot of thoroughly mixed sludge into a centrifuge tube. Adjust pH to appropriate extraction pH. Add solvent to the sample and homogenize with an ultrasonic probe. Centrifuge the sample and extracts at 3,000 rpm for 30 secs. Withdraw solvent	More labor and equipment intensive than other methods.	Appears to be most suitable for sludges. Centrifugation step probably eliminates filtration problems encountered in previous method.

TABLE 1 (Continued)

METHOD	REFERENCE(S)	BRIEF DESCRIPTION	DISADVANTAGES	ADVANTAGES
Sludge/ Sediment Method (Homogeniza- tion/Centrifu- gation) (Continued)	Midwest Research Institute (1979)	layer from the tube with a pipette. Solvent is filtered through Na_2SO_4 for removal of excess water. Extraction of the solids is repeated at least 2 or 3 times. Extracts are combined for conventional clean up and concentration.		
Municipal Sludge (GPC Pre- treatment)	Convery et al (1980)	Sludge sample is elevated to high pH and extracted with methylene chloride. Extract undergoes Gel Per- meation Chromatography (GPC) to remove lipids high molecular weight fatty acids and hydro- carbons. Elutant from GPC is passed through silica gel column to remove saturated hydro- carbons from polar or aromatic organics. Extracts are then in- jected into GC/MS. Acid fraction can be treated similarly.	High capital cost for equipment (GPC); longer more com- plicated procedure.	Reduces levels of materials which cause interferences; provides higher resolution.
Acid/Neutral Extraction for Sludges and Complex Wastes	DeWalle & Chian (1979)	Extract with methylene chlorine at pH 2. Save raffinate for base ex- traction. Treat acid/ neutral fraction with GPC. Discard eluate with lipids (inter- ference). Split acid/ neutral fraction in half, treating one portion with florisil for separation of sat- urated hydrocarbons from priority neutrals; treat other GPC fractions with cesuim silicate to separate acids (phenols) from pri- ority neutrals. Acid fraction may be methylated before analysis by GC/MS Method produces 3 neutral fractions which may be analyzed singly or com- bined by GC/MS. Pesticides and PCB's are analyzed in the neutral fraction. Base fraction is raised to pH 12, dried and concentrated, then run on GC/MS.	More complicated and labor intensive than other procedures.	Good detection limits, i.e., approximately 1 $\mu\text{g/L}$ for ex- tractables in wastewater and 5-10 $\mu\text{g/L}$ for sludges.

- (2) Separatory funnel methods are only suitable for samples with low suspended solids concentrations, i.e. treatment plant effluents;
- (3) For wastewater samples with high suspended solids or sludges; continuous extraction, steam distillation, homogenization/filtration, homogenization/centrifugation or the more complex GPC pretreatment procedures should be employed. A variety of factors including desired detection limits, nature of sample matrix, interferences, existing laboratory and labour capabilities, etc, will influence method selection.

2.2 Fate Of Organics In Wastewater Treatment Plants

2.2.1 Biodegradability

Persistent trace organic contaminants are compounds that are resistant to conventional biological treatment. Ludzack and Ettinger (1960) reviewed information available on aerobic stabilization of chemical compounds. In general, they found that resistance to biological treatment increased as molecular weight increased, or as the chemical structure became more highly branched (i.e. hydrogen atoms were substituted by alkyl or aryl groups). Atoms other than carbon in a chain frequently increased resistance to biodegradation, with oxygen having the greatest effect, followed by sulphur and nitrogen. Chambers et al (1936) investigated the ability of phenol-adapted activated sludge cultures to degrade 106 aromatic compounds. Only eleven aromatics caused no measurable oxygen uptake. Resistant compounds were trihydric phenols, benzylalcohols and nitro- or chlorobenzoic acids. Biodegradation was generally affected by substituent groups (e.g. chloro, nitro, alkyl groups) and their position on the benzene ring. Pitter (1976) tabulated the

degradabilities of 94 aromatic, 15 hydroaromatic and 14 aliphatic compounds in acclimated activated sludge cultures. He found 19 compounds resistant to degradation; these compounds were dinitrobenzenoids and benzene sulphonic acids. Aniline was found to be fairly biodegradable, after 120 hours in the aeration basin, aniline was reduced by about 94.5% based on COD reduction.

Baird et al (1977) studied twelve aromatic amines in activated sludge. With the exceptions of N, N-dimethylamine, all compounds showed significant reductions of 20%-100%, after 6 hours of aeration. No suspected carcinogenic metabolites of benzidine were found to survive the activated sludge process.

Thom and Agg (1975) considered the degradability of numerous organic compounds by biological treatment processes, and classified them as easily degradable, degradable after suitable acclimatization, or resistant to degradation. Resistant organics included herbicides, pesticides, PCB's, pentachlorophenol, organometallic compounds, ABS and other surfactants. Compounds removable after acclimatization included phthalate esters, di- and tri-chlorinated hydrocarbons, xylenes and other benzenoid compounds. Their list included 33 easily degradable, 37 resistant and 138 degradable after acclimatization compounds.

Thom and Agg (1975) listed aniline as one organic that should be easily biodegradable in a sewage treatment plant. Methyl-2-mercaptobenzothiazole examined in this study would be expected to be resistant to biodegradation because 2-mercapto-benzothiazole was listed by Thom and Agg (1975) in the non-biodegradable group.

Tabak et al (1980) used 7 day static cultures followed by three weekly subcultures to assess the biodegradability of organic priority pollutants. The compounds, which are divided into 10 classes, were identified as exhibiting significant degradation with rapid adaptation; significant degradation with gradual adaptation; significant degradation with gradual adaptation followed by a dead adaptive process (toxicity) in subsequent subcultures; or not significantly degraded under test conditions. Each compound was tested at 5 mg/L and 10 mg/L concentrations. The ten categories listed were as follows:

<u>Category</u>	<u>Example of Compounds in Category</u>
Phenols	Phenol, 2,4-dichlorophenol, p-chlorocresol
Phthalate Esters	Diethyl Phthalate, Di-n-octyl Phthalate
Naphthalenes	2-Chloroaphthalene, Acenaphthene
Monocyclic Aromatics	2,4-Dichlorobenzene, Nitrobenzene, Ethylbenzene, 2,6-Dinitrotoluene
Polycyclic Aromatics (PAH's)	Anthracene, Phenanthrene, Pyrene, Chrysene
Halogenated Ethers	Bis (2-chloroethyl) Ether, 4-Bromodiphenyl Ether
PCB's	Arochlor 1016, 1232, 1242, 1254, 1260
Nitrogenous Organics	N-Nitrosodiphenylamine, Isophorone, Acrylonitrile
Halogenated Aliphatics	1,2-Dichloroethane, Chlorodibromomethane, Tetrachloroethylene
Organochlorine Insecticides	Aldrin, Chlordane, Heptachlor, p,p'-DDT.

Diethyl phthalate and di-n-octyl phthalate were found by Tabak et al (1980) to undergo significant degradation after a rapid adaptation for the former and a gradual adaptation for the latter.

Sato and Akiyama (1972) investigated biodegradation of volatile organic acids by activated sludge treatment. Formic acid was observed to be oxidized to the extent of 68%, whereas acetic, propionic, butyric, valeric and caproic acids were reduced by only 29%-38%. It should be noted however, that considerably higher removal for the aforementioned organics are reported elsewhere. Giger et al (1976) found volatile acids were reduced by 5 to 10 fold after activated sludge treatment, although they did not specify if the removal was due to biodegradation or air-stripping.

Saeger et al (1976) examined the degradation of three aliphatic adipic acid diesters and a 1, 3-butylene glycol adipic acid polyester by activated sludge. Primary degradation of 67-99 plus % was observed for the three adipic acid diesters after 24 hours of aeration. Inadequate analytical procedures prevented analysis of the glycol adipic acid polyester. Gledhill (1975) investigated the ability of activated sludge to degrade 3,4,4'-trichlorocarbanilide (TCC). At a 10 hour HRT and 200 µg/L of TCC, acclimatization of the activated sludge was readily achieved. TCC is hydrolyzed in activated sludge to form p-chloroaniline (PCA) and 3,4-dichloroaniline (DCA). The PCA produced was completely metabolized, while only 50% of the DCA was degraded under the operating conditions. Joel and Grady (1977) examined the influence of aniline on nitrification in an activated sludge system. At a 7 day SRT, aniline was completely degraded and had no inhibitory influence on nitrifying bacteria in the activated sludge. Baird et al (1977) observed that aniline at 20 mg/L had an inhibitory effect on the oxygen uptake rate in activated sludge. Aniline was depleted by 54% after 6 hours aeration.

Saleh et al (1980) examined chlorinated hydrocarbon pesticides and chlorophenoxy herbicides in municipal wastewater. Neither activated sludge nor trickling filter treatment resulted in significant removal of these chlorinated organics. The herbicide 2, 4-D was reduced by between 16% and 55%. Transformation of the chlorinated hydrocarbon pesticides was observed; aldrin was converted to dieldrin, and DDT was converted to DD and DDE.

Tucker et al (1975) indicated that biphenyls with one or two chlorine atoms were readily biodegradable, but resistance to degradation increased with the number of chlorine atoms, especially when the number exceeds five. They observed that when compared to biphenyl the PCB's Arochlor 1242 and Arochlor 1254 were reduced by only 26% and 15%, respectively. Kaneko et al (1976) noted that PCB's caused an increase in the oxygen uptake rate and a change in the micro-flora of activated sludge at concentrations as low as 1 mg/L. Neither activated sludge nor anaerobic digestion resulted in significant degradation of the PCB designated Kanechlor 500. They did observe that up to 60% of the PCB was lost by volatilization after 20 hours of aeration.

2.2.2 Identification Of Organic Contaminants In Wastewater Treatment Plants

Garrison et al (1977) described a classification system for organic compounds in water and wastewater. A total of 24 classes were identified, based on functional groups in the organic compounds, except for miscellaneous non-volatile compounds. Compounds within these 24 major classes were reviewed as to the number of times they have been reported in raw and treated municipal wastewater and industrial wastes.

Fine and Rounbehler (1976) detected dimethylnitrosamine (DMN) at 3 µg/L in the final effluent of a South Baltimore sewage treatment plant. They make no comments on whether the level of DMN in the final effluent is reduced from the concentration in raw sewage, or whether the DMN is generated during treatment of the sewage.

Unchlorinated primary and secondary municipal effluents were examined by Katz et al (1972) with UV and carbohydrate analysis. Seventy-seven peaks were detected in primary effluent at concentrations less than 100 µg/L, and 38 peaks were found in secondary effluent at levels less than 20 µg/L. Many of the peaks were common to both samples, suggesting that a number of compounds passed through the treatment system at reduced levels. Two peaks were higher in secondary effluent than in the primary, indicating their production during treatment. Among the compounds identified by Katz et al (1972) were an unsubstituted and a substituted uracil, and several methyl-xanthine isomers. A number of simple sugars were also identified in both primary and secondary effluent.

Pitt et al (1974) were able to identify 56 organic compounds in primary effluent and 20 organics in unchlorinated secondary effluent from the Oak Ridge National Laboratory area. Compounds identified in greatest concentrations were o-phthalic acid, 4-hydroxylphenylacetic acid, 5-acetylamino-6-amino-3-methyl uracil, phenylalanine and 7-methylxanthine. Many more complex organic acids were also noted in the primary effluent. Most organics identified in the secondary effluent samples were also noted in the primary effluent, suggesting the compounds were somewhat resistant to biodegradation.

Certain volatile organic compounds are more apt to be stripped from the aeration tank mixed liquor than to be biodegraded or absorbed onto solids. Compounds in this volatile class typically include chloroform, dichloropropane, trichloroethane, trichloroethylene, tetrachloroethylene and dichlorobenzene. As a means of estimating the volatility of the organic priority pollutants, EPA's Municipal Environmental Research Laboratory (MERL) has estimated the Henry's Law constants for these organics in wastewaters (Convery, et al, 1980). Similarly, Matter-Muller et al (1980) considered removal mechanisms in biological treatment plants, and estimated that as much as 72% of compounds such as trimethylbenzene and dichlorobenzene may be lost from aeration tanks by air stripping.

Harrison et al (1975) reviewed polyaromatic hydrocarbons (PAH's) in wastewater treatment plants. Primary sedimentation was found to remove about 33% of PAH's (range 20%-80%). Biological treatment removed about 90% of influent PAH's, whereas alum and alum plus polymer removed 50% and 90% respectively of benzo(a) pyrene from synthetic sewage. Powdered activated carbon was also reported as being effective for PAH removal in wastewater. Removals of nine PAH's by sedimentation and biological treatment were tabulated. Most prevalent PAH's were fluoranthene, benzo(a)pyrene, benzo(a)anthracene, benzo(i) fluoranthene and benzo(b) fluoranthene. Concentrations were reduced from the microgram per litre level to the submicrogram per litre level after biological treatment. Fluoranthene was the most resistant to biological degradation.

Pitt et al (1975) in later work reported that 103 unknown organic compounds were detected in primary effluents and 20 unknown organics found in secondary effluents in addition to the compounds previously reported.

Garrison et al (1976) identified trace organics in raw wastewater and effluents from biological and physical/chemical treatment. Activated sludge reduced concentrations of main trace organics by 3-to 5-fold while physical/chemical treatment resulted in a 10- to 100-fold decrease in concentrations. Main components in raw sewage were long chain aliphatic fatty acids, caffeine, nicotine, several aliphatic and aromatic hydrocarbons, chloesterol, coprostanol and phthalate esters. Activated sludge treatment caused the appearance of five new compounds thought to represent intermediates from LAS biodegradation. Physical/chemical treatment caused formation of two new oxygen-containing fatty acids, thought to result from biological growth in activated carbon columns. The 80 identified compounds (plus other unidentified organics) represented only volatile methylene chloride-extractable compounds, which constitute less than 25% of the total organics in wastewater.

Giger et al (1976) found that aliphatic hydrocarbons similar to No. 2 fuel oil (n-alkanes in C_{11} to C_{14} range) were the dominant organics in primary effluents. In secondary effluents, hydrocarbons of a higher boiling range, centering on n-heptadecane, were predominant. They concluded that biological treatment was ineffective for degradation of C_{14} to C_{20} alkanes. Removal may be accomplished by adsorption of the higher saturates on activated sludge flocs, whereas volatile and non-polar compounds may be removed by air-stripping in the aeration tanks. Twenty-two aromatic hydrocarbons were detected in primary and secondary effluents, mostly methyl-and ethyl-substitute benzenes. P-dichlorobenzene was the most common chlorinated benzene.

The fate of 19 organic pollutants through a wastewater renovation plant was followed by Van Rensburg et al (1980). The process train involved pre-denitrification, chemical coagulation/precipitation, sedimentation, nitrification, sedimentation, pre-chlorination, dual media filtration, activated carbon treatment and final chlorination. Chemical coagulation was found to reduce the majority of the trace organics; activated carbon eliminated most of the compounds remaining after the additional treatment steps. Only (bis) chloroethylether and dichlorobenzene survived the treatment process, but at greatly reduced concentrations.

Burlingame et al (1976a) investigated removal of trace organics from secondary effluents by tertiary treatment, consisting of chemical coagulation, clarification, dual media filtration and chlorination. Samples were evaluated before activated carbon treatment. Chlorinated benzenes in the secondary effluent were not observed in the tertiary effluent. Six new unidentified compounds resulted from tertiary treatment. Organic concentrations following tertiary treatment were the same order of magnitude as in the secondary effluent.

Reinhard et al (1979) examined the ability of advanced waste treatment (AWT) to remove trace organics from secondary effluent at the Water Factory-21 facility in Orange County, California. Lime precipitation reduced PCB concentrations, ammonia stripping lowered the concentration of many low molecular weights, non-polar volatile organics, and activated carbon reduced a broad range of chlorinated and unchlorinated hydrocarbons. They concluded that AWT can remove about 90%-95% of the total organic matter remaining in secondary effluents. Chlorination was observed to increase levels of trihalomethane and other undesirable chlorinated organics.

Chow and David (1977) examined the resistance of organic compounds in biological and physical/chemical effluents to activated carbon treatment. Resistant compounds included chlorinated hydrocarbons, long chain highly unsaturated and substituted aliphatic acids, aromatic amines and phenolic compounds. The compounds in both biological and physical/chemical effluents, resistant to carbon adsorption, were similar.

Use of the DuPont PACT (powdered activated carbon) process for trace organic removal was described by Hutton and Temple (1979). The PACT process out performed activated sludge for all of the 14 chemicals tested. At a 100 ppm carbon dosage, a slight increase in efficiency was noted for benzene, whereas a large increase was noted for 2, 4-dichlorophenol. The bench scale test unit achieved better results than did the full scale unit.

Convery et al (1980) reported that considerable progress has been made in establishing the absorptive capacity of activated carbon for removal of trace organics. In this regard, adsorption isotherms have been determined by EPA for most of their 129 priority pollutants.

Organic compounds in secondary effluents were examined by Waggot and Wheatland (1977). Selected organics were classified as being easily degradable, slowly degradable or persistent. They considered that effluents from biological treatment would be more complex than untreated effluent. Traces of the organics will remain after treatment since their concentration will frequently be a factor in bacterial activity, and also because metabolic products from bacterial growth and condensation products from endogenous respiration will also be present. The data of Pitt et al (1975) and Garrison et al (1976) tend not to support this concept. Biodegradable compounds, included short and long chain unsaturated aliphatic acids, cresols, phenol and glycerol. Slowly degradable chemicals consisted of straight

chain ABS compounds, trichloroethylene, trichlorophenols, dibutyl phthalate, ethylamine, biphenyl and others. Within the persistent organics were branches chain ABS compounds, Dieldrin, pentachlorophenol and PCB's among others.

Mori et al (1978) examined the volatile organic compounds in a municipal primary effluent. Identification of 51 compounds were made. Compounds found in the highest concentrations were terpineol, p-cresol and menthol.

Menka et al (1974) reported on soluble organics in effluents from trickling filter, extended aeration and stabilization ponds. Fulvic acid and protein were the major components of the total COD. Compounds identified in an ether-extractable fraction were 8 fatty acids, 19 n-alkane hydrocarbons, 2 alkyl benzenes, 6 aromatics and triethyl phosphate. Sheldon and Hite (1978) noted that municipal effluents were characterized by high concentrations of stearols fatty acids and fatty acid esters.

Shannon et al (1976) examined PCB concentrations in 33 wastewater treatment plants in Ontario. Primary treatment plants removed an average of 50% of the influent PCB's whereas secondary plants removed an average of 66%. PCB concentrations in plant influents ranged from the detection limit up to 1.8 µg/L. In digester sludges, PCB's ranged from 23 to 6700 µg/L, in one sludge cake, the level was 12,600 µg/L. Little degradation of PCB's was observed; rather, the removal mechanism was established as adsorption onto solids. Experimental results of Lawrence and Tosine (1977), Kaneko et al (1976) and Bergh and Peoples (1977) support this observation. Bergh and Peoples (1977) followed the concentration of PCB's through a trickling filter plant. Concentrations at various stages are summarized in Table 2. The majority of the PCB's were removed in grit chamber solids and sludge sent to the anaerobic

digester. Herbst et al (1977) observed that three PCB's were not degraded by activated sludge and were distributed between the water phase and sludge solids, at hydraulic residence times up to 5 days.

Table 2

Distribution Of PCB's In Wastewater Aqueous And Solid Phases

AQUEOUS PHASE		SOLID PHASE	
PROCESS STREAM	CONCENTRATION (mg/L)	SAMPLE DESCRIPTION	CONCENTRATION (mg/kg)
Raw Sewage	0.03-0.47	Grit Solids	48-532
Grit Chamber		Solids From T.F.	
Effluent	0.03-0.11	Rock	220
Primary Effluent	0.07-0.33	Digester Supernatant Solids	210-261
Tricking Filter			
Effluent	0.05-0.08	Dried Anaerobic	
Secondary Effluent	0.02-0.05	Sludge	238-1700
Filtrate From			(mean - 765)
Sludge Drying Bed	0.27		

Daniels et al (1979) rated organic pollutant removal processes for their ability to treat 17 common industrial organic compounds. Processes including steam stripping, oil-water separation, media filtration, biological oxidation and carbon adsorption were judged as removing most, some or little (or none) of each compound.

A preliminary report of a study commissioned by the U.S. EPA (Feiler, 1980) concerning the fate of priority pollutants in publicly owned treatment works has been issued. Two plants in this report were studied, as preparations for a 40 plant survey; one plant received a heavy industrial input, and the other almost none. Solvents and phthalate esters were in highest concentration in the influents, whereas bis-(2-ethylhexyl) phthalate and PAH's predominated in primary sludge. Priority pollutants were analyzed for frequency of occurrence, concentrations in influent, effluent, and primary and secondary sludges.

Mass balances at the two plants were also attempted. The report suggested that removal of organic priority pollutants in raw sewage can be accomplished by adsorption onto solids, air stripping of volatiles, chemical oxidation, especially during disinfection, and biodegradation.

Feliciano (1980) reports that in an EPA study of 50 POTW's (34 plants have been analysed to date) six organic priority pollutant compounds (benzene, chloroform, methylene chloride, bis (2-ethylhexyl) phthalate, tetrachloroethylene and toluene) were found in nearly all wastewaters, including plants receiving only municipal sewage. In addition, 1, 1-dichloroethylene, ethylbenzene, butyl benzyl phthalate, di-n-butyl phthalate, diethyl phthalate and trichloroethylene were frequently found in the wastewater samples.

Erickson and Pellizzari (1979) examined sludges (mostly anaerobically digested) from nine U.S. cities. A total of 35 chlorinated compounds were found, but not all were found at all locations (i.e., some were site specific). Of the thirty-five compounds, 16 were identified as mostly of the chloroaromatic variety.

Ongerth and DeWalle (1980) reviewed the behaviour of organic priority pollutants in three Seattle, Washington POTW's. Thirteen chlorinated volatile organics, 6 PAH's, 7 chlorinated or alkyl benzenes, 4 phthalates, 4 substituted phenols and two others were found in raw wastewater and primary and secondary effluents. Toluene was observed as having the highest concentration in raw wastewater at 250 µg/L. Compounds present in all samples included 8 commercial solvents and diethylphthalate. Ongerth and DeWalle (1980) noted that the chlorinated C_1 - C_2 compounds, chlorinated or alkyl benzenes, and phenolics all displayed relatively high correlation with the fraction of industrial waste input, whereas phthalates were unrelated to the industrial contribution.

2.2.3 Effects of Chlorination on Trace Organics

Pfaender (1977) noted the various reactions that chlorine may undergo with organics in wastewater. Oxidation reactions, producing chloride ion predominate; for example, aldehydes are oxidized by HOCl to carboxylic acids. Chlorine can react with unsaturated hydrocarbons, nitrogen containing organics and aromatics to form organochlorines. Organo-nitrogen compounds are chlorinated rapidly, especially with more basic nitrogen compounds, and phenol and anisole are readily chlorinated at pH 7.

Glaze et al (1973) reported the formation of new chlorinated compounds in a municipal biological effluent with chlorine dosages as low as 10 mg/L of available chlorine for 1 hour. New organo-chlorine compounds were estimated to be in the 1-50 µg/L range, although no identification of compounds was made. Under super-chlorination conditions (i.e. 2,000-4,000 mg/L of Cl₂), Glaze and Henderson (1975) and Glaze et al (1976) found that 39 new peaks, representing new organo-chlorine compounds, were detected in secondary effluent, mostly in the 10-40 µg/L range. One compound, 3-chloro-2 methylbutylene was found at 285 µg/L. Many new chlorinated derivatives of benzene, toluene and benzyl alcohol were noted in the 10-40 µg/L range. In 1975, Glaze and Hamilton suggested that total organic-bound chlorine could be as high as 3,000-4,000 µg/L. In a later publication, however, Glaze et al (1976) indicated that superchlorination increased the total organic-bound chlorine by about an order of magnitude, i.e. from about 10-40 µg/L to 200-900 µg/L.

Pitt et al (1974) and Jolley (1975) examined chlorination of municipal, primary and secondary effluents using radioactive chlorine. One percent of the applied chlorine dosage was associated with stable organochlorine compounds (not chloramines). A total of 62 new organochlorine compounds were noted in primary and secondary effluents. In a secondary effluent sample, 17 of the new peaks (mostly chlorinated aromatic organics) were identified at levels between 0.24 and 4.3 µg/L. The compound with the highest concentration was 5-chlorouracil. The concentrations in Jolley's study were generally lower than those found by Glaze et al (1976). Major findings of Pitt et al (1974) and Jolley (1975) were that the yield of organochlorine compounds increased as the chlorine contact time increased and that hypochlorite solution and chlorine gas gave essentially equivalent results.

Garrison et al (1976) examined the effect of chlorination on organic compounds in lime-clarified raw sewage. Chlorination caused the disappearance of a number of compounds including caffeine, nicotine, x-terpineol, salicylic acid and three mono-unsaturated fatty acids. A number of polychlorinated ethanes, chlorocyclohexane and other unidentified compounds appeared as a result of chlorination.

Effects of chlorination on volatile organics in a municipal primary effluent were observed by Mori et al (1978), who found 19-21 new compounds resulting from chlorination. Only 0.01% of chlorine applied to the primary effluent ended up as volatile organochlorine compounds. This value is considerably less than the 1% indicated by

Jolley (1975), but the latter study included non-volatile compounds as well. In the study by Mori et al (1978), 40% of the organically bound chlorine in primary effluent was attributed to chlorination. Only chlorobenzene, 1, 3-dichlorobenzene and α -chlorotoluene were positively identified at concentrations of 7-10 $\mu\text{g/L}$.

Harrison et al (1975) reviewed the fate of PAH's during disinfection. Mixed results were achieved in the tests they reviewed; their conclusion was that initial PAH concentrations and chlorine dosages are important in PAH destruction.

2.2.4 Trace Organics In Industrial Wastewater Treatment

Garrison et al (1977) noted the number of times various classes of organic contaminants were reported in industrial effluents. Keith (1974) examined organic pollutants in wastewaters from two petrochemical plants, two petroleum refineries, two chemical companies and one synthetic rubber manufacturer. The types of waste treatment system, if any, for each company were noted, as were the organic compounds and concentrations in the waste effluents. Compounds were detected in the $\mu\text{g/L}$ to mg/L range.

Jungclaus et al (1976) identified the trace organic compounds in two tire manufacturing plant wastewaters. At one plant, the major effluent contaminants were oleic and stearic acid, at a combined concentration of 56 mg/L , and toluene at 10 mg/L . Waste treatment consisted of a catchment area for oil, grease and suspended solids removal followed by a lagoon with a 5 d HRT. At the second plant, also utilizing a lagoon system, benzothiazole and 2-mercapto-benzothiasole at 60 $\mu\text{g/L}$ and 30 $\mu\text{g/L}$, respectively, were the major contaminants.

Burlingame et al (1976b) followed organic pollutants in a petroleum refinery served by a treatment scheme involving an API separator, Pasveer oxidation ditch, clarifier and waste stabilization lagoon. Major constituents present in the wastewater were high molecular weight n-alkanes, alkylbenzenes and alkylated phenols and anisoles.

Keith (1976) compared treatment of Kraft paper mill wastewaters by physical/chemical and biological processes. Samples were collected at various locations in the treatment systems. In total, 61 compounds were identified in wastewaters from both plants. Most prevalent compounds were guaiol, vanillin, methyl isopimerate, methyl abietate, methyl dehydroabietate, and methyl neoabietate, all at the 1-4 mg/L range. Methyl dehydroabietate was not removed by either type of treatment. A new compound, methyl-13-abieten-18-oate, was formed as a result of treatment, in both cases at the 1 mg/L level. Although 85-90% reductions in BOD were achieved with both treatment systems, the physical/chemical system removed 80-85% of the TOC, whereas, the biological system removed only 60-65%. This discrepancy may be due to the increase in total fatty acids in the biological system thought to arise from metabolism of aquatic biota in the aerated lagoon.

Jungclaus et al (1978) examined the effluent of a specialty chemicals manufacturer. This wastewater was treated by neutralization in equalization tanks, trickling filtration and final clarification. A total of 123 organic compounds were identified in the treatment plant effluent, river water to which the effluent discharged and river sediments. Compounds in the effluent ranged from the $\mu\text{g/L}$ to several

hundred mg/L levels. Organics present in the highest concentrations in the effluent were acetone, methanol, 2-butanone, toluene and 2, 4, 4'-trichloro-2'-hydroxydiphenylether.

Lamb et al (1979) examined removal of 8 organics in synthetic coal conversion wastewater by lab-scale activated sludge at 5, 10 and 20 d detention periods. Removals at 10 and 20 d retention times for selected contaminants ranged between 87.2-99.5% and 91.9-99.5%, respectively. Aniline, at a feed concentration of 5 mg/L was reduced by 87.8% and 92.2% at 10 d and 20 d detention times, respectively.

3.0 Phase 1 - Facilities and Procedures

3.1 Wastewater Treatment Plant Description

The treatment plant selected for the sampling program is a conventional secondary treatment plant designed to treat an average hydraulic flow of $3.1 \times 10^3 \text{ m}^3/\text{day}$. Seventy-four percent of the flow is from the municipality and miscellaneous industries with the remaining 26% from an organic chemical manufacturing plant. The design BOD_5 loading for the activated sludge system is 1,300 kg/day. Presently, about 40% of the total BOD_5 loading to the plant is from the organic chemical manufacturing facility. A schematic diagram for the plant is presented in Figure 1. Design data are summarized in Table 3.

Wastewater characteristics and plant operational data for the treatment plant are summarized for the period of October 1 to December 21, 1979, in Table 4. During this period the plant achieved 88% BOD_5 removal and 79% suspended solids removal. The phosphorus removal system was not in continuous operation during October through December.

3.2 Sampling Procedures

The wastewater treatment plant was sampled on two occasions, i.e. December 4 and December 11, 1979. Twenty-four hour composite samples were collected at the following locations: (See Figure 1)

- A - Municipal Wastewater
- B - Industry Wastewater
- C - Combined Municipal/Industry Wastewater
- D - Secondary Effluent Prior to Chlorination

TABLE 3
DESIGN DATA FOR WASTEWATER TREATMENT PLANT

$$\text{Design Flow} = 3.1 \times 10^3 \text{ m}^3/\text{day} \quad \left\{ \begin{array}{ll} 2.3 \times 10^3 \text{ m}^3/\text{day} & \text{Municipal} \\ 0.8 \times 10^3 \text{ m}^3/\text{day} & \text{Industry} \end{array} \right.$$

UNIT	DETAILS
Equalization	Industry wastewater equalized prior to discharge to plant. Municipal wastewater not equalized.
Primary Treatment	Two (2) 12.2 m diameter x 2.4 m SWD clarifiers. Design surface loading at average flow = 13.3 m/day.
Aeration Basins	Four (4) aeration basins with total volume of 1,360 m ³ . Four (4) mechanical aerators at 15 HP each. Design BOD ₅ loading = 1,300 kg/day.
Secondary Clarifiers	Two (2) 13.7 m diameter x 2.1 m SWD clarifiers. Design surface loading at average flow = 10.5 m/day. Return sludge capacity = 100 to 150% of average flow.
Chlorine Contact Chamber	Two (2) 9.1 m x 1.8 m x 1.4 m SWD chambers in parallel. Retention time at average flow = 22.5 min.
Digestion	One (1) primary digester 9.1 m diameter x 6.7 m SWD and one (1) secondary digester 9.1 m diameter x 6.7 m SWD. Digesters are not being heated or mixed. Used for sludge storage only.

FIGURE 1 SCHEMATIC OF WASTEWATER TREATMENT PLANT
SHOWING SAMPLING LOCATIONS

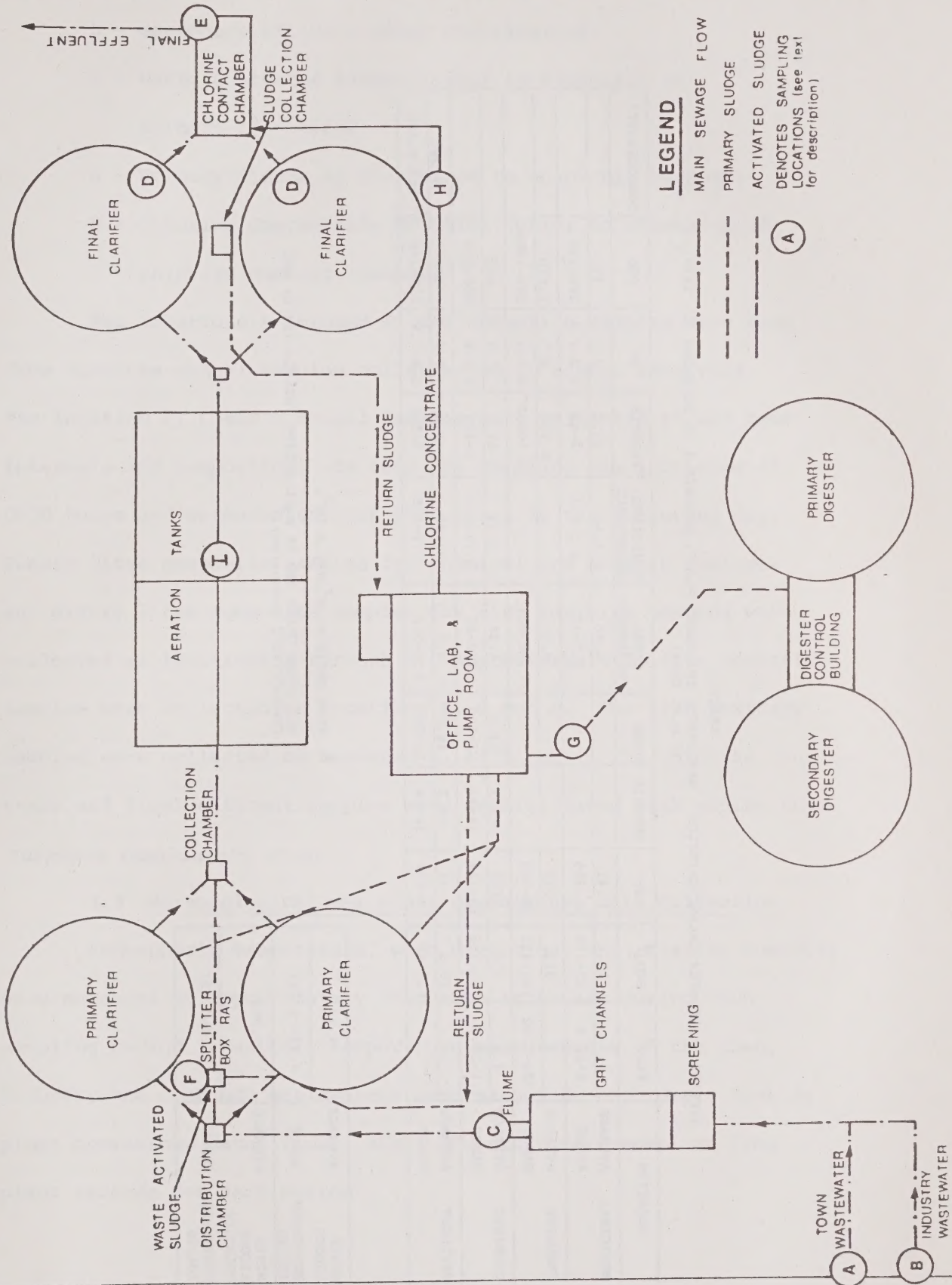


TABLE 4
AVERAGE WASTEWATER CHARACTERISTICS - WASTEWATER TREATMENT PLANT, OCTOBER 1 TO DECEMBER 31, 1979.
(M.O.E. DATA)

LOCATION	FLOW ¹	BOD ₅ ²	SS	AMMONIA	TKN	TOTAL PHOSPHORUS	DISSOLVED PHOSPHORUS	PHENOLS	pH	COD	CONDUCTIVITY
MUNICIPAL	AVERAGE	3.3	101			6.98	4.66	13.7	7.5	372	
	RANGE	.6-10.9	82-155	45-305		3.7-11	3.1-6.1	3-42	7.2-7.9	280-420	
INDUSTRY	AVERAGE	.5	313			4.75		9,900	6.7	1,020	
	RANGE	.228-.782	160-410	36-305		.36-8.1		1-39000	4.6-8	800-1300	
COMBINED	AVERAGE	4.1	134	49.2	62.0	6.38	3.44	61	7.4	440	
	RANGE	1.1-10.7	95-155	30-72	27-130	2.2-12	.78-5.6	1-250	6.9-8	400-560	
EFFLUENT	AVERAGE		16.5	46.2	46.0	8.0	1.86	1.8	7.4	136	7,300
	RANGE		6.0-45	34-54	15-75	0.9-5.2	.72-4.5	.5-5.0	6.8-7.9	110-190	6,200-8,600

MIXED LIQUOR	AVERAGE	4,433
SUSPENDED SOLIDS	RANGE	3,234-6,227
MIXED LIQUOR	AVERAGE	3,068
VOLATILE SOLIDS	RANGE	1,909-4,137

1 FLOW UNITS = $m^3/day \times 10^3$.

2 ALL OTHER UNITS ARE IN mg/L EXCEPT PHENOLS (ug/L) AND CONDUCTIVITY (umhos/cm).

- E - Secondary Effluent after Chlorination
- F - Waste Activated Sludge (prior to discharge to primary clarifier)
- G - Primary Sludge as Discharged to Anaerobic Digester
- H - Chlorine Concentrate Solution (prior to discharge to chlorine contact chamber)

For locations A through E, the composite samples were made from discrete manual samples collected at 30 minute intervals. The location F, G and H manual samples were collected at six hour intervals and composited. On each day sampling was initiated at 0800 hours and extended through 0730 hours on the following day. Twenty litre composite samples for chemical and organic analyses and eighty litre composite samples for fish toxicity testing were collected at locations A through E. Approximately 5 litre composite samples were collected at locations F, G and H. The fish toxicity samples were collected on December 4, 1979 only. The chlorine concentrate and final effluent samples were dechlorinated with sodium thio-sulphate immediately after.

3.3 Meteorological and Plant Operational Data Collection

Atmospheric temperature, wind direction, and relative humidity were measured at approximately four hour intervals during each sampling period. Periodic temperature measurements of the town, industry and combined wastewaters were also made each day. Routine plant operations data (flows, MLSS, DO, etc.) were compiled from plant records for each period.

3.4 Routine Analyses

The composite samples were analyzed by the MOE Laboratory in Rexdale for the routine parameters listed in Table 5.

TABLE 5

ROUTINE ANALYSES CARRIED OUT ON TREATMENT PLANT SAMPLES

Total Suspended Solids	Total Kjeldahl Nitrogen
Volatile Suspended Solids	Ammonia Nitrogen
Total Organic Carbon	Nitrate
Total Carbon	Nitrite
Chemical Oxygen Demand	Total Phosphorus
Biochemical Oxygen Demand (5 day)	Phenols

3.5 Trace Organic Extractions and Analyses

Prior to initiating the sampling program, a meeting was held with representatives of the organic chemical plant that discharges to the wastewater treatment. During this meeting, the company provided preliminary information on raw materials and products. Because of the diversity of raw materials and products and the potential for other trace organics entering the town wastewater from domestic and other industrial sources, it was decided to use a general extraction procedure for all of the samples. This general procedure, as provided by the MOE (OTC) Laboratory, is presented in Appendix A. This procedure is basically an adaptation of a published EPA procedure (EPA, 1977).

For the first set of samples collected on December 4, the general protocol described in Appendix A was followed for extraction of the liquid samples. The solvent utilized was dichloro-methane (methylene dichloride). Neutral-base and acid extractions were performed serially with 100, 50 and 20 ml volumes of methylene dichloride. It was found that the solvent formed a gelatinous emulsion with the suspended solids in some samples. By applying mechanical agitation with a glass stirring rod and hot water to the outside of the separatory funnel, some of the emulsion could be broken. However, solvent recoveries were low, i.e. 60-75%. It is generally desirable to have solvent recoveries in the order of 90% or greater.

After a review of available or modified extraction methods for sludges (see Literature Review of Extraction Methodologies), it was decided to use a steam-distillation procedure for the Phase 1 sludge samples. This modified Nielsen-Kryger procedure is described by Veith and Kiwus (1977) and is generally suitable for liquids, sediments and tissue samples. Fifty mls of primary sludge samples were diluted to 200 mls with TOC free water and distilled for two hours into 4 mls of benzene. Separate neutral-base and acid distillations were carried out on each sample. Two hundred mls aliquots of the waste activated sludges were distilled directly for two hours into 4 mls of benzene. Separate neutral-base and acid distillations were carried out on each sample. The dilution of the primary sludge samples was necessary to prevent excessive foaming.

The crude liquid extracts for each sample were filtered through Na_2SO_4 to remove any traces of water. The extracts were then roto-vaped to approximately 4 mls. The final concentrates were made up to 10 mls with methylene dichloride. The sludge extracts were filtered through Na_2SO_4 to remove traces of water and the final concentrates made up to 10 ml volume with benzene. All extracts were then delivered to the MOE (OTC) Laboratory for Gas Chromatography/Mass Spectrometry (GC/MS) analyses. Details on the actual procedures utilized for GC/MS analyses are published elsewhere (EPA, 1977) and are available from the OTC Laboratory.

In some runs, a 800 ml aliquot of organic free distilled water was put through the same extraction procedures to ensure all reagents used were pure.

4.0 Phase 2 - Facilities And Procedures

The Phase 2 sampling of this study utilized bench scale activated sludge and anaerobic digester reactors.

4.1 Nitrification Reactors Sampling

Two bench scale nitrification reactors were sampled. Reactor A received a 2:1 by volume mixture of town/industry wastewater whereas Reactor B received a 5:1 mixture. Each reactor consisted of a temperature controlled aeration chamber equipped with a mixed feed tank, a secondary clarifier and sludge return pump and a final effluent storage tank. A schematic diagram of the reactor unit is shown in Figure 2.

Mean operating conditions for the nitrification reactors at the time of sampling are noted in Table 6. The temperature and Solids Retention Time (SRT) in the aeration tank were controlled to simulate winter operation. The hydraulic residence time (HRT) was 24 hours when the first two sets of samples were collected, and 12 hours when the last set of samples was taken.

The reactors were fed on a daily basis with the feed being made up from continuous 24 hour composite samples of primary clarified municipal wastewater and pretreated and equalized industrial wastewater. The samples were collected at locations A and B respectively as shown in Figure 1.

Samples of the nitrification reactors influent, effluent and waste activated sludge were collected for trace organic analyses on three separate dates (February 27, March 4 and April 21, 1980).

The influent samples to each reactor A and B were divided into two aliquots: the first aliquot of approximately 25 liters was used for extractions. On April 21 this sample was subdivided to give two replicate samples. The pH of these samples was raised to 10 ± 0.02 using 6N sodium hydroxide. The samples were filtered through Whatman #1 filter paper. The filter papers and solids were placed into a 1000 ml wide mouth glass bottle and frozen until extracted. A 1000 ml sample of the filtrate was stored at 4°C until extractions could be performed. The second aliquot was used for routine parameter analyses (Table 5).

The entire effluent from both A and B nitrification systems was collected for the same 24 hour period as the influent samples were being collected. An aliquot of the effluent was removed and the pH raised to 10.0 ± 0.2 using 6N sodium hydroxide and a pH meter. On April 21, this sample was divided into two replicates. Samples were filtered through Whatman #1 filter paper and stored at 4°C until the extractions were performed. The solids fraction and filter papers were discarded. An aliquot of the original effluent samples was submitted to the MOE Laboratory for routine parameter analyses.

The small daily volume of activated sludge being wasted from the nitrification systems necessitated the accumulation of the sludge over an extended period in order to collect enough volume for analysis. The total waste sludge volume from each system was stored at 4°C until about 2 litres had been collected.

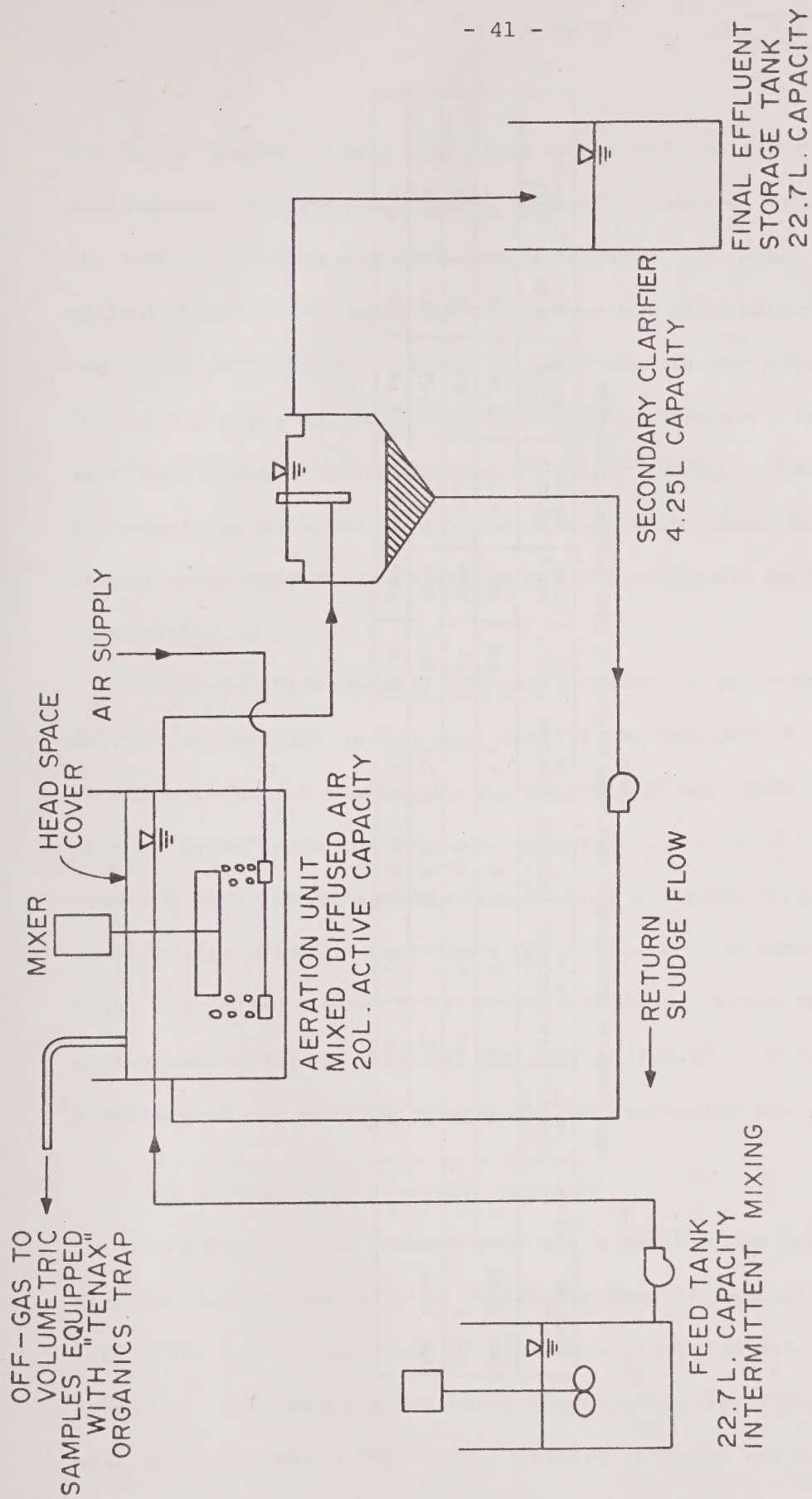


FIGURE 2 — SCHEMATIC DIAGRAM OF LABORATORY SCALE
BIOLOGICAL NITRIFICATION TREATABILITY UNIT

TABLE 6
MEAN OPERATING CONDITIONS OF NITRIFYING REACTORS AT TIME OF SAMPLE COLLECTION

SAMPLING DATE	SYSTEM	HRT IN AERATION (HOURS)	SRT (DAYS)	TEMP. IN AERATION (°C)	DO IN AERATION (MG/L)	PH IN AERATION	MLSS (MG/L)	MLVSS (MG/L)	PERCENT VOLATILE	F/M LB BOD/LB MLVSS	SVI (ml/g)	O ₂ UPTAKE RATE mg O ₂ /g VSS/h
FEB. 27/80	A	24	50	8.0	6.1	7.6	3520	2890	82.1	0.11	58	6.3
MAR. 4	B	24	50	8.1	6.4	7.6	3670	2900	78.9	0.08	75	3.5
APR. 21/80	A	12	50	5.2	8.6	7.4	6490	5035	77.7	0.07	104	7.6
	B	12	50	5.6	8.2	7.7	6370	4900	77.0	0.06	157	6.5

The daily wasted volumes were then composited and mixed. Two 500 ml samples were removed for routine parameter analyses (Table 5), and the remaining litre was used for extractions. On April 21, each collected sample was subdivided into two 500 ml fractions for replicate extractions. The pH of each fraction was raised to 10.0 ± 0.2 using 6N sodium hydroxide and a pH meter. The samples were then filtered using Whatman #1 filter papers. The filter papers and solids were placed in a 1,000 ml wide mouth glass bottle and frozen until they could be extracted. The filtrate fraction was discarded.

For aeration chamber off-gas sampling, a metal cover was fabricated over and sealed over each of the two nitrification unit aeration tanks. A volumetric gas sampler (Nuteck Model 221) equipped with a "tenax" organics trap was used to draw on 11 liter air sample from the aeration tank head space through a copper tube. In order to eliminate organics that might be present in the ambient air being fed to the reactors, an activated carbon filter was installed on the aeration tank air feed line. The "Tenax" organics traps were submitted to the MOE-OTC Laboratory for extraction and analyses.

4.2 Anaerobic Digester Sampling

As part of the Phase 2 program, a bench scale anaerobic digester reactor was sampled during the week of February 4 to 11, 1980. The reactor was made of stainless steel and was 22 liters in volume. The reactor was batch loaded every day with raw sludge made up of 3:1 ratio (by volume) primary to waste activated sludge. The primary sludge was taken from the pilot clarifier used for treating town influent only. The waste activated sludge was taken from the full scale treatment plant (location F in Figure 1).

Digester operational conditions during the sampling period are summarized in Table 7.

TABLE 7
DIGESTER OPERATING CONDITIONS DURING ORGANICS SAMPLING

Operating Conditions	Temperature Retention Time Loading Rate	35°C 26 days 0.704 g VS/L.d
Sludge Characteristics	Total Solids Volatile Solids pH Alkalinity Volatile Solids	10.9 g/L 54% of Total 6.8 2,570 mg/L as CaCO_3 510 mg/L as CH_3COOH
Overall Performance	Volatile Solids Reduction Gas Production	68% 0.86 L/g VS Added

A 500 ml sample of the digester feed sludge mixture and digester effluent was taken each day and stored at 4°C until a 7 day composite had been collected. 500 ml aliquots of each composite were analyzed for routine parameters. The pH of each of the remaining samples was raised to 10.0 ± 0.2 using 6N sodium hydroxide and a pH meter. Two duplicate 1,000 ml aliquots, were taken from each composite. These samples were filtered using Whatman #1 filter papers. The filter paper and solids were placed in 1,000 ml wide mouth glass bottles and frozen until they could be extracted. A 850 ml sample of the filtrate for each sample was saved and stored at 4°C until extractions could be performed.

A digester gas sample was collected during the week of composite sampling. A 22 liter specialized gas sampling bag was connected to the digester gas line and allowed to fill over a 48 hour period. The bag was then sealed and forwarded to the MOE-OTC Laboratory for gas analyses.

4.3 Extraction Procedures

As discussed later, six specific organic compounds were selected for monitoring during Phase 2. These included aniline, benzothiazole, 2-methylmercaptobenzothiazole, diphenylamine, diethyl phthalate and dioctyl phthalate. As a result of the problems encountered with extraction of some of the Phase 1 samples (particularly liquid samples), extraction procedures were modified somewhat for Phase 2. In addition, some replicate and spiked sample analyses were conducted in order to check reproducibility and recovery of the extraction and analytical methodology. The Phase 2 analyses were carried out by the Analytical Services Section, Inland Waters Directorate, Ontario Region at Burlington. Again, GC/MS procedures were utilized. Extraction procedures are shown in Figure 3.

4.3.1 Liquid Sample Extractions

After transferring 800 ml of liquid sample to 1 L separatory funnel, sample pH was adjusted to 10 ± 0.2 using 6N NaOH and a pH meter. The liquid was extracted serially with three portions of 80, 30 and 30 ml of distilled-in-glass methylene dichloride. Each extract was shaken vigorously for at least 2 minutes. The phases were allowed to settle for 3 minutes or until the two phases were distinct. The solvent was separated from the aqueous layer and then filtered through pre-washed glass wool and pre-extracted

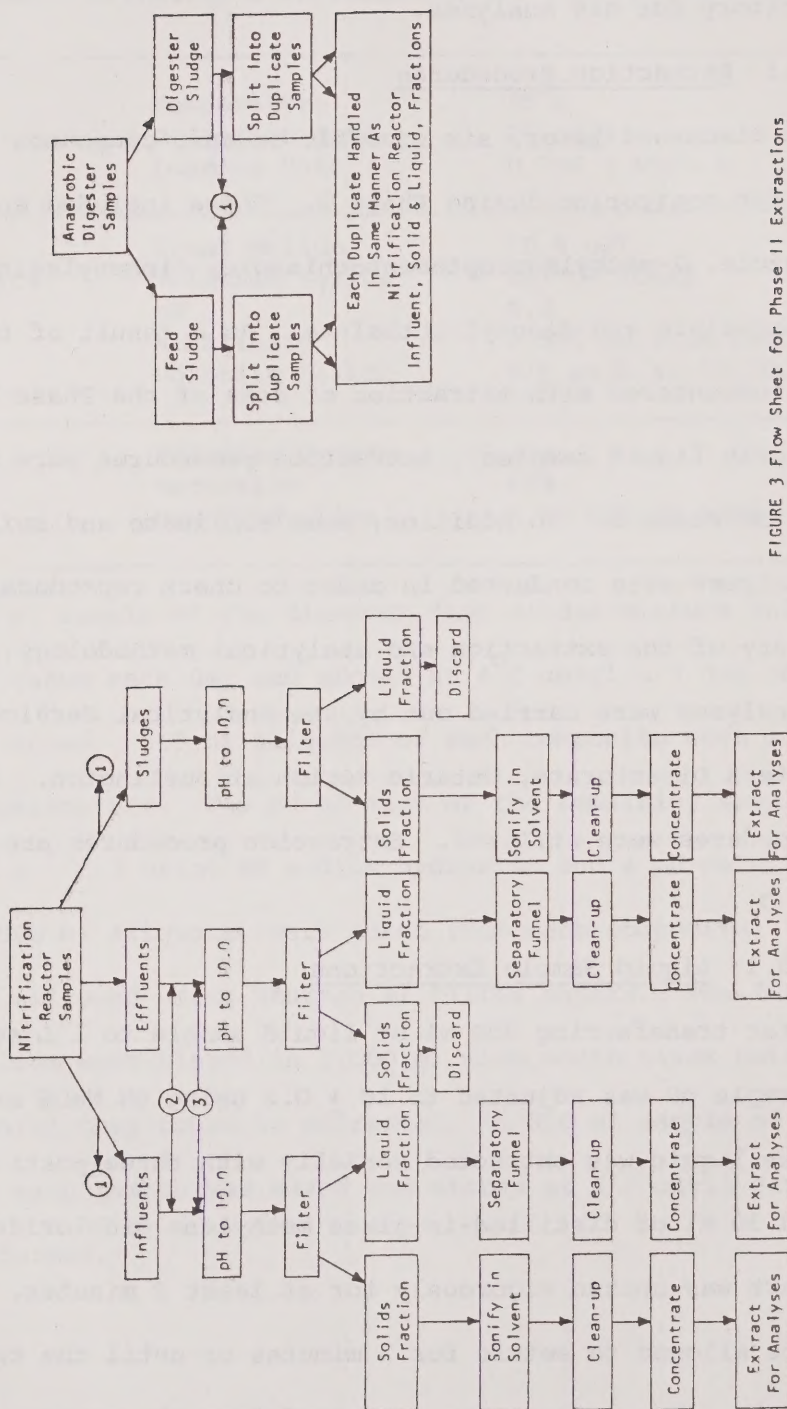


FIGURE 3 Flow Sheet for Phase II Extractions

1. Sample for Routine Parameters
2. Spiked with d_5 Nitrobenzene for Feb. 27 and March 4 samples.
3. Duplicate samples run on April 21, one set spiked with six compounds plus d_5 nitrobenzene, other set treated in usual manner.

granular sodium sulphate (Na_2SO_4). The combined methylene chloride extracts were rotary evaporated to near dryness using water pressure to create a vacuum and a water bath at $25^\circ\text{C} \pm 5^\circ\text{C}$.

The concentrated extract was then transferred to a calibrated centrifuge tube. The sample was rinsed into the tube with the same solvent using 2 ml, 1 ml and 1 ml aliquots. The extract was then diluted to 10 ml volume with solvent and capped with a teflon lined cap. Extracts were stored in a refrigerator until analyses were performed.

4.3.2 Solids Sample Extractions

After the solids had been separated from the liquid phase by filtration through a Whatman # 1 filter paper, the filter papers and solids were placed in a 1,000 ml wide mouth glass bottle and frozen prior to extraction.

The extraction procedure commenced by transferring 250 mls of methylene dichloride directly into the sample bottle containing the solids and filter papers. The sample was then subjected to disruption using a Bronson Model 350 cell sonifer with a 12.5 mm solid horn. A pulse intensity of 8 with a 60% on, 40% off pulse duration was used for a total time of 10 minutes. The sample bottle was immersed in a tapwater cooling bath during sonification.

The sonified solids-solvent mixture was filtered through a pre-washed Whatman #1 filter paper. This extract was then filtered through a pre-extracted granular sodium sulphate funnel to remove any traces of water.

The extract was rotary evaporated to near dryness using water pressure to create a vacuum and a water bath at $25^{\circ}\text{C} \pm 5^{\circ}\text{C}$. The concentrated extract was then transferred to a calibrated 15 ml centrifuge tube. The sample was rinsed into the tube with solvent using 2 ml, 1 ml and 1 ml aliquots. The concentrated extract was then diluted to 10 ml with solvent and capped with a glass or teflon lined cap. The extracts were stored at 4°C until analysis on GC/MS could be performed.

4.3.3 Duplicate and Spiked Samples

In order to run a preliminary check on reproducibility, selected samples were extracted and analyzed in duplicate. These included all solid and liquid fractions of the anaerobic digester samples (feed and digested sludge).

To check the recovery of the extraction and analytical procedure, a duplicate set of the April 21 nitrification reactor samples (solid and liquid fractions of the influent, liquid fraction of the effluent and solid fraction of waste activated sludge) were spiked with known concentrations of the six test compounds plus a tracer, d_5 nitrobenzene. The spikes were added in amounts calculated to increase the final extract concentration by 10 ng/ μL (assuming 100% recovery). In addition, a TOC free water sample and two TOC free water samples spiked at 10 and 50 ng/ μL of the six test compounds (final extract concentration) were run through the same extraction and analytical procedures.

4.4 Analytical Procedures

The nitrogen containing compounds analyses (aniline, diphenylamine, benzothiazole and methylmercapto-benzothiazole) were performed on a capillary gas chromatograph equipped with a flame ionization detector. The separation was achieved on a 25 metre methyl silicone (SP-2100) fused silica wall open tubular column programmed from 50°C to 270°C at 2°/minute. Under these conditions the detection limit was 5 ng/μL in the extract.

Phthalates were run by separate analysis on a GC/MS. The detection limit for the diethyl and dioctyl phthalates was 1 ng/μL in the extract.

5.0 Results and Discussion - Phase 1

5.1 Operational Data

The wastewater treatment plant operational data for the two sampling dates of December 4, 1979 and December 11, 1979 are summarized in Table 8. The plant was hydraulically overloaded (i.e. design average flow = $3.1 \times 10^3 \text{ m}^3/\text{day}$) with some bypassing occurring on both days. Plant parameters, F/M and SRT, indicated that the activated sludge system was operating at the low end of the conventional mode. Chlorine was being fed to the final effluent to give a total chlorine dosage of 2.3 mg/L. No total available chlorine residual was detected in the final effluent. The average chlorine residual in the concentrate line was 95 mg/L.

The routine parameter results are summarized in Table 9. For the two days the plant averaged 82% BOD₅ removal and 61% suspended solids removal. The reduced suspended solids removal was probably due to the hydraulic overloading condition. The plant was not nitrifying as evidenced by the relatively high ammonia levels in the effluent (i.e. 30 mg/L and 42 mg/L). By comparing the data of Table 9 with that of Table 4, it can be concluded that the plant performance during the sampling was fairly representative of its long term performance.

5.2 Trace Organic Analyses

A total of thirty-five samples were extracted and submitted to the MOE-OTC laboratory. Twelve of these samples were analysed by Gas Chromatograph/Mass Spectrometry (GC/MS) with a view to identifying the most prevalent organic compounds occurring at the wastewater treatment plant. The remaining samples were analysed by GC alone. In this phase, more compounds other than those listed in Table 10 had been identified. However, the peaks for such compounds were of very low magnitude and were, therefore, not tabulated.

TABLE 8

OPERATIONAL DATA FOR THE WASTEWATER TREATMENT PLANT DURING ORGANIC SAMPLING

DATE	TOWN AVG. FLOW ($m^3 \times 10^3$)	TOWN PEAK FLOW ($m^3 \times 10^3$)	INDUSTRY AVG. FLOW ($m^3 \times 10^3$)	MLSS (mg/L)	MLVSS (mg/L)	F M	SRT (Days)	SVI	RETURN SLUDGE ($m^3 \times 10^3$)	WASTE SLUDGE ($m^3 \times 10^3$)	CHLORINE FEED (kg)	CHLORINE RESIDUAL EFFLUENT (mg/L)	CHLORINE RESIDUAL CONCENT. (mg/L)
Dec. 4/79	3.77	710.0 ¹	0.57	5050	3670	0.10	11.0	98	3.47 (81 %)	0.032	12.2 (2.8 mg/L)	0.0	95
Dec. 11/79	4.10	710.0 ²	0.41	5600	3775	0.12	10.9	83	3.52 (78 %)	0.036	9.5 (2.1 mg/L)	0.0	95

¹ Bypassing occurred at 9:30 to 9:45 p.m. on December 3, 1979, and 8:30 to 8:45 a.m. on December 4, 1979.

² Bypassing occurred at 3:15 to 3:45 p.m. on December 11, 1979, and 8:15 to 9:15 a.m. on December 11, 1979.

Sludge hauled from digester in December = $0.173 \times 10^3 m^3$

Average D0 in aeration tank = 3.4 mg/L

Minimum D0 in aeration tank = 2.6 mg/L

Maximum D0 in aeration tank = 4.1 mg/L

NOTES:

On December 4, 1979, red dye was prevalent in the Town influent at 20:00 to 21:00 hours. Green dye was evident in the Town influent at 1:00 and 5:00 hours on December 5, 1979. On December 11, 1979, red dye was prevalent in the Town influent from 14:00 to 16:30 hours. Grey dye was evident at 2:00 to 3:00 hours on December 12, 1979.

TABLE 9

SUMMARY OF ROUTINE PARAMETER ANALYSES AT THE WASTEWATER TREATMENT PLANT (Dec. 4 and 11, 1979)

	DATE	SS	VSS	TOTAL ORGANIC CARBON	TOTAL CARBON	COD	BOD ₅	TKN-N	NH ₃ -N	NO ₂ -N	NO ₃ -N	TOTAL-P	PHENOL (ppb)
Town Influent	Dec. 4	115	89	70	157	233	84	27	15	0.1	0.1	5.2	270
	Dec. 11	114	94	81	160	213	53	25	13	0.01	0.1	5.6	
Industrial Influent	Dec. 4	273	96	300	350	1208	381	140	94	1.4	2.6	4.3	62400
	Dec. 11	177	83	340	380	1045	227	255	154	0.16	12	3.4	
Combined Influent	Dec. 4	150	97	110	194	364	139	46	29	0.03	0.2	5.2	3000
	Dec. 11	117	88	120	190	336	71	67	40	0.02	0.6	4.9	
Pre-chlorinated Final Effluent	Dec. 4	92	52	33	114	107	20	38	30	0.02	0.2	3.5	120
	Dec. 11	43	31	34	110	103	11	62	42	0.03	0.3	3.4	
Chlorinated Final Effluent	Dec. 4	59	37	38	118	112	21	38	30	0.02	0.3	4.0	200
	Dec. 11	44	33	33	110	108	15	62	42	0.03	0.3	3.4	
Chlorine Concentrate	Dec. 4	77	48	40	100	-	-	35	22	0.02	0.1	4.1	0
	Dec. 11	51	41	44	90	328	82	50	38	0.06	0.1	3.8	
Primary Sludge	Dec. 4	3072	1860	1500	1790	4277	-	310	50	0.06	0.1	95	2240
	Dec. 11	16.1% ¹	18.2% ²	-	-	98352	-	2700	180	0.18	0.1	880	
Return Sludge	Dec. 4	12476	9244	4400	4560	13170	-	940	38	0.02	0.1	410	315
	Dec. 11	11824	9028	4600	4400	10762	-	1050	50	0.02	0.2	370	

All values in mg/L unless indicated otherwise.

¹ Total Solids² Total Volatile Solids

TABLE 10
MATRIX OF ORGANIC COMPOUNDS DETECTED IN WASTEWATER AND SLUDGE SAMPLES COLLECTED DURING PHASE 1.

LOCATION COMPOUND	DECEMBER 4, 1979 SAMPLES						DECEMBER 11, 1979 SAMPLES					
	C ¹ ACID	C N-BASIC	D N-BASIC	E N-BASIC	F N-BASIC	F ACID	G ACID	H N-BASIC	C N-BASIC	D N-BASIC	E N-BASIC	H N-BASIC
Benzaldehyde						X	X					
Hydroxylamine- α -decyl*							X					
Methylmercaptobenzothiazole	X		X	X	X	X	X	X		X	X	X
Diphenylamine	X	X		X	X	X	X	X	X	X	X	X
Di-Octyl Phthalate	X	X	X	X	X	X	X	X	X	X	X	X
Di-Ethyl Phthalate	X	X	X	X				X	X		X	
Other Phthalates			X		X	X	X	X			X	
Benzothiazole	X	X	X	X	X	X	X	X	X	X	X	X
Phenylaziridine*					X							
Phenols	X	X				X			X			
Methyl Indolizine*					X	X						
Diethylthio-Benzo-thiazole	X											X
Aniline		X		X					X		X	X

¹ See Figure 1 for sample locations.

* Tentative Identification.

C = Combined Influent
D = Pre Chlorinated Effluent
E = Chlorinated Effluent
F = Waste Activated Sludge
G = Primary Sludge
H = Chlorine Concentrate Line

In the sludge samples, major peaks were found for diethyl phthalate, methylmercapto benzothiazole, benzothiazole and diphenylamine. The compounds were common to all the sludge samples analysed. The acid extract of the December 4 primary sludge sample showed the presence of benzaldehyde, methyl phenol and methyl indolizine, while the basic extracts of waste activated sludge contained trimethyldihydroquinoline and phenylaziridine. All the sludge samples showed the presence of a number of hydrocarbons.

The wastewater extracts demonstrated the presence of a number of the same compounds found in the sludges. The basic extracts of the selected samples were analysed by GC/MS. A few acid extracts were analysed by gas chromatography alone using a flame ionization detector.

Benzothiazole, diethyl phthalate, dioctyl phthalate, diphenylamine and methylmercaptobenzothiazole were noted in almost every extract. Other compounds encountered in the wastewater extracts were phenol, aniline and other phthalates.

The results presented herein are in agreement with previous organic monitoring results obtained for the subject plant (MOE-OTC unpublished data). For example, previous analyses on the plant effluent in 1977 and twice in 1979 indicated the presence of aniline, benzothiazole, methylmercaptobenzothiazole and diphenylamine at detectable levels.

Several of the compounds identified in this study have also been encountered in other monitoring programs. For example, Jungclaus et al (1978), monitored the effluent of a trickling filter treating

wastewater from a speciality chemicals manufacturing plant in the U.S. The plant had a somewhat similar product mix to the one monitored in this study. Benzothiazole, analine, several different phenols and dioctyl phthalate were detected in the effluent and the receiving water. Over 45 different trace organic compounds were detected in the U.S. treatment plant effluent

5.3 Effect of Chlorination on Trace Organics

Samples of pre- and post-chlorinated effluent and chlorine concentrate collected on two different days were analysed qualitatively for organic compounds (Table 10). 2-Methylmercapto-benzothiazole, dioctyl phthalate, benzothiazole and diphenylamine were detected in all samples analyzed. Since the concentrate water is drawn from the secondary effluent and fed through the chlorinator and subsequently returned to the chlorine contact chamber, it might be expected to contain some of the same compounds as the unchlorinated and chlorinated effluent samples. It is interesting to note on December 4 (Table 9), that the concentrate did not contain phenols at detectable levels even though pre- and post-chlorinated effluents contained relatively high levels of phenol. Apparently, the phenolic groups in their chemical structure were oxidized by the high chlorine levels (95 mg/L) in the concentrate.

5.4 Selection of Organics to be Monitored in Phase 2

It was decided upon the completion of Phase 1 sampling, to limit the number of organic materials to be monitored in Phase 2. The following criteria were used in selecting a "short-list" of organic compounds:

- (1) compounds should be at high enough concentrations so that they could be readily detected in influent, effluent and sludge samples. If these compounds were also major raw material products or by-products of the organic chemical plant, this would give further assurance of detectable levels;
- (2) compounds should be organic chemicals of some environmental concern, e.g. persistent toxic substance, hazardous polluting substance or potential hazardous polluting substance in the Great Lakes Water Quality Agreement of 1978 (IJC, 1978) or one of the EPA Priority Pollutants (Keith, 1979);
- (3) analytical procedures should be as uncomplicated as possible, i.e. gas chromatography alone versus GC/MS;
- (4) the compounds selected should show up as a group either in the acid or neutral-base extract, therefore, eliminating the time consuming double extraction procedure;
- (5) analytical standards should be available for the selected compounds.

The compounds listed in Table 10 were evaluated with respect to the above criteria and as a result, the following compounds were selected for the Phase 2 monitoring:

- (1) Diphenylamine
- (2) Dioctyl phthalate
- (3) Diethyl phthalate

- (4) Methylmercapto benzothiazole
- (5) Benzothiazole
- (6) Aniline

Information concerning the use, toxicity and properties of the six selected compounds has been summarized in Appendix B. The phthalates are listed as EPA priority pollutants (Keith and Telliard, 1979), in the MOE Blue Book (1978), and as persistent toxic substances in the Great Lakes Water Quality Agreement (IJC, 1978). Aniline is listed on the Michigan DNR Critical Materials Register (CMR) and most of the other compounds have or are currently being screened by Michigan DNR for possible inclusion on the (CMR).

5.5 Results of Fish Toxicity Tests

Static 96-hour bioassays using juvenile rainbow trout were run on the first set of samples (December 4) collected from the treatment plant. Separate bioassays were carried out in 80 litre samples of town only wastewater, industry wastewater, combined wastewater, pre-chlorinated effluent and chlorinated effluent. In all of the bioassays, 100% fish mortality occurred within 16 hours. This was subsequently attributed to the relatively high ammonia content in the samples (See Table 4).

A subsequent set of samples of effluents were collected from the nitrification reactors (i.e. reactors receiving 2:1 and 5:1 town: industry wastewater feeds) during December 10 through 13, 1979. Fish mortality for the 2:1 reactor (100%) effluent was 100% within 22 hours, whereas 0% mortality after 96 hours was observed for the

5:1 reactor. The higher mortality for the 2:1 reactor may be attributable to the higher ammonia levels in its effluent (i.e. 3-9 mg/L as compared to <2 mg/L in the 5:1 reactor). Without further investigation, it is impossible to determine what other factors, or combination of factors, caused the mortality in the 2:1 effluent.

6.0 Results and Discussion - Phase 2

6.1 Nitrification Reactor Performance

A summary of the routine parameter analyses for the 2:1 and the 5:1 bench-scale nitrification reactors on the three sampling days is presented in Table 11. With the exception of the 2:1 reactor on April 21, both the 2:1 and the 5:1 reactor were nitrifying on all sampling days as evidenced by the effluent ammonia and nitrate levels in Table 11. On April 21, the 2:1 reactor was not nitrifying or achieving any significant degree of BOD removal. Apparently, the reduced HRT of 12 hours and the low temperature of 5.6°C (see Table 6) resulted in process failure in the 2:1 nitrification reactor.

On all sampling days, the two reactors demonstrated a high degree (>90%) of phenol removal. With the exception of the 2:1 reactor on April 21, BOD₅ and SS removals by the reactors were in the range of 85%-95% plus. Total organic carbon removals were also in excess of 90%.

6.2 Anaerobic Digester Performance

The feed and the digested sludge leaving the bench-scale anaerobic digester was sampled over the period of February 4 to 8. The feed to this digester was made up of three parts of primary sludge from a pilot scale primary clarifier and one part of waste activated sludge taken from the full scale WPCP.

Digester performance during the sampling period has been summarized previously in Table 7. Over the sampling period, the digester was operating with a hydraulic retention time of 26 days,

TABLE 11
SUMMARY OF ROUTINE PARAMETER ANALYSES FOR THE BENCH SCALE NITRIFICATION UNITS.

	DATE	SUSPENDED SOLIDS	VOLATILE SUSPENDED SOLIDS	TOTAL ORGANIC CARBON	TOTAL CARBON	COD	BOD ₅	TKN-N	NH ₃ -N	NO ₂ -N	NO ₃ -N	TOTAL-P	PHENOL (ppb)
2:1 TOWN/INDUSTRY FEED	Feb. 27	150	93	160	240	502	340	36	20	1.0	9.9	5.1	85
	Mar. 4	150	98	200	276	702	338	41	23	5.5	8.1	5.0	5,500
	Apr. 21	221	141		57	318	155	30	16	-	-	3.8	725
2:1 TOWN/INDUSTRY EFFLUENT	Feb. 27	29	13	10	80	38	7	2.0	0.2	0.02	36	0.98	8
	Mar. 4	32	20	17	91	61	10	5.0	2.0	0.02	34	0.86	11
	Apr. 21	122	55		39	314	141	23	17			3.0	12
2:1 TOWN/INDUSTRY WASTE ACTIVATED SLUDGE COMPOSITE	Feb. 27	12,000	3,000	1,300	1,500	4,608	NS	335	18	0.05	0.8	77	140
	Mar. 4				NO SAMPLE ANALYZED								
	Apr. 21	5,560	4,300	-	-	4,699	-	1200	35	-	-	270	112
5:1 TOWN/INDUSTRY FEED	Feb. 27	146	99	120	200	443	244	38	21	1.8	1.6	6.2	110
	Mar. 4	149	106	142	224	510	252	43	24	0.35	0.2	7.0	3,750
	Apr. 21	106	74		35	220	117	22	13			3.3	400
5:1 TOWN/INDUSTRY EFFLUENT	Feb. 27	21	11	9	68	32	5	1.6	0.10	0.01	33	1.5	5
	Mar. 4	12	8	10	70	36	5	1.8	0.1	0.01	32	1.0	8
	Apr. 21	37	22			45	18	1.6	0.2			2.3	6
5:1 TOWN/INDUSTRY WASTE ACTIVATED SLUDGE COMPOSITE	Feb. 27				NO SAMPLE ANALYZED								
	Mar. 4	8,800	3,000	1,200	1,400	3,775	-	290	3.8	0.02	2.7	86	7
	Apr. 21	4,998	3,796	-	-	4,361	-	700	30	-	-	190	40

All values in mg/L except where indicated.

TABLE 12

COMPARISON OF EXTRACT CONCENTRATIONS (ng/ μ L) FOR DUPLICATE
SAMPLES FROM THE ANAEROBIC DIGESTER FEED AND EFFLUENT STREAMS

Sample	Replicate	Aniline		Benzothiazole		2-Methylmercapto benzothiazole		Diphenylamine		Diethylphthalate		Diethyl phthalate	
		Conc.	% CV ⁽¹⁾	Conc.	% CV	Conc.	% CV ⁽¹⁾	Conc.	% CV	Conc.	% CV ⁽²⁾	Conc.	% CV ⁽¹⁾
Digester Feed (Solid Fraction)	1	<5 ⁽²⁾		33		35	106	<5		43		467	
	2	7		7	92	<5	to 141	-		46		37	
Digester Feed (Liquid Fraction)	1	5		<5		6		<5		5		<1	
	2	<5		<5		61		<5		560		5	
Digester Effluent (Solid Fraction)	1	35	106	<5	83	<5		<5		11		162	
	2	<5	to 141	19	to 141	<5	-	-		31		66	
Digester Effluent (Liquid Fraction)	1	<5		<5		27		<5		184		4	
	2	8		<5		6	90	<5		25		9	

Notes: 1) % CV = percent coefficient of variation = $\frac{\text{standard deviation}}{\text{means}} \times 100\%$.

2) < = less than. This sign is used to imply that the compound was detected by the GC/MS, however, its concentration was below the quantification limit of the GC/MS instrument used.

TABLE 13

EXTRACT CONCENTRATIONS (ng/μL) IN BLANK AND

SPIKED TOC - FREE WATER SAMPLES

SAMPLE	ANILINE	BENZOTHIAZOLE	METHYLMERCAPTO- BENZOTHIAZOLE	DIPHENYL- AMINE	DIETHYL- PHTHALATE	DIOCTYL- PHTHALATE
BLANK		<1.0	<1.0	<1.0	<1.0	<1.0
TOC - FREE WATER	N.P.	N.P. ⁺	N.P.	N.P.	N.P.	N.P.
TOC - FREE WATER PLUS 10 ng/μL SPIKE	3.5 (35) [*]	5.5 (55)	6.1 (61)	6.5 (65)	6.2 (62)	<1.0 (<10)
TOX - FREE WATER PLUS 50 ng/μL SPIKE	20.5 (41)	25.2 (50)	26.7 (53)	26.3 (53)	26.8 (54)	9.1 (18)

+ N.P. = NOT PRESENT.

* THE NUMBER IN THE PARENTHESIS IS % RECOVERY.

TABLE 14

PERCENT RECOVERY ATTAINED IN THE EXTRACTS PREPARED WITH THE ORIGINAL AND
 THE SPIKED SAMPLES TAKEN FROM THE TWO BENCH SCALE NITRIFICATION REACTORS
 THE SPIKE SAMPLES WERE PREPARED BY INCREASING THE COMPOUND CONCENTRATIONS IN
 THE ORIGINAL SAMPLES BY 10 ng/ μ L PER COMPOUND

SAMPLE	ANILINE			BENZOTHIASOLE			2-METHYLMERCAPTO			DIPHENYLAMINE			DIETHYLPHTHALATE			DIOCTYLPHTHALATE		
	A	(a)	B	(b)	C	(c)	A	B	C	A	B	C	A	B	C	A	B	C
2:1 LIQ. INFL.	54.5	12.3	-420	<5	12.2	72/122	27.0	17.0	-100	<5	8.8	38/88	<5	10.4	54/104	<5	5	50/-50
2:1 LIQ. INFL.	<5	97.2	922/972	<5	47.5	425/475	6.8	18.1	113	13.5	34.6	211	5.6	<5	-6/-56	30.2	50.2	200
2:1 LIQ. EFFL.	<5	<5	50/-50	<5	<5	50/-50	<5	5.0	0/50	<5	5.9	9/59	<5	8.7	37/87	<5	<5	50/-50
2:1 WAS ^(d)	<5	<5	50/-50	<5	<5	50/-50	18.1	47.3	292	<5	22	170/220	<5	<5	-50/50	48.6	68.4	198
5:1 LIQ. INFL.	12.6	<5	-76/-126	<5	<5	50/-50	20.0	<5	-150/-200	<5	<5	50/-50	<5	5.0	0/50	<5	<5	50/-50
5:1 SOLID INFL.	57.7	19.1	-386	<5	49.2	442/492	5.0	22.1	171/221	56	22.1	165	5.2	10.4	52	51.7	39.0	-127
5:1 LIQ. EFFL.	<5	<5	50/-50	<5	<5	50/-50	<5	<5	50/-50	5	5.7	7/57	<5	<5	50/-50	<5	8.5	35/85
5:1 WAS	<5	<5	50/-50	<5	<5	50/-50	100	11.0	10	<5	9.0	40/90	<5	<5	50/-50	11.2	25.4	142

NOTES: (a) A = CONCENTRATION MEASURED IN THE ORIGINAL SAMPLE (ng/ μ L).

(b) B = CONCENTRATION MEASURED IN THE SPIKED SAMPLE (ng/ μ L).

(c) C = PERCENT RECOVERY (%):

- WHEN BOTH A AND B = > 5 ng/ μ L; C = ((B-A)/10)x100%

- WHEN A < 5 ng/ μ L AND B > 5 ng/ μ L; C = ((B-5)/10)x100% AND IS TABULATED ABOVE THE SLASH; C = ((B-0)/10)x100% AND IS TABULATED BELOW THE SLASH

- WHEN A > 5 ng/ μ L AND B < 5 ng/ μ L; C = ((5-A)/10)x100% AND IS TABULATED ABOVE THE SLASH; C = ((0-A)/10)x100% AND IS TABULATED BELOW THE SLASH

- WHEN BOTH A AND B < 5 ng/ μ L; C = ((5-0)/10)x100% AND IS TABULATED ABOVE THE SLASH; C = ((0-5)/10)x100% AND IS TABULATED BELOW THE SLASH

(d) WAS = WASTE ACTIVATED SOLIDS.

TABLE 15

RESULTS OF SPECIFIC COMPOUND ANALYSES FOR 2:1

NITRIFICATION REACTOR INFLUENT, EFFLUENT AND WASTE ACTIVATED SLUDGE SAMPLES

SAMPLE LOCATION	DATE	SPECIFIC COMPOUND CONCENTRATION IN ORIGINAL SAMPLE ($\mu\text{g/L}$)					
		ANILINE	BENZOTHIASOLE	2-METHYLMERCA- PTOBENZOTHIASOLE	DIPHENYLAMINE	DIETHYL- PTHALATE	DIOCTYL- PTHALATE
2:1 TOWN/INDUSTRY FEED (LIQUID FRACTION)	FEB. 27/80	100	138	<63	75	25	13
	MAR. 4/80	9,625	213	763	63	4,125	13
	APR. 21/80	682	<63	338	<63	<63	<63
2:1 TOWN/INDUSTRY FEED (SOLID FRACTION)	FEB. 27/80	<1 ^a	8.4	(56)	10	(92)	35 (235)
	MAR. 4/80	3	4	(24)	6	(41)	25 (163)
	APR. 21/80	<2	9	(39)	3	(12)	2 (10)
2:1 TOWN/INDUSTRY WASTE ACTIVATED SLUDGE COMPOSITE (SOLID FRACTION)	FEB. 27/80	(^a <7) ^b	(10)	(72)	(13)	(28)	(343)
	MAR. 4/80	(^a <23)	(^a <23)	(64)	(^a <23)	(^a <23)	(524)
	APR. 21/80	(^a <18)	(^a <18)	(112)	(^a <18)	(^a <18)	(175)
2:1 TOWN/INDUSTRY EFFLUENT (LIQUID FRACTION)	FEB. 27/80	<63	<63	88	<63	50	13
	MAR. 4/80	<63	<63	75	<63	13	<13
	APR. 21/80	<63	<63	<63	<63	<63	<63

^b VALUES IN PARENTHESIS ARE CONCENTRATIONS EXPRESSED ON DRY WEIGHT BASIS ($\mu\text{g/kg}$).^a VALUES NOT IN PARENTHESIS ARE CONCENTRATIONS EXPRESSED IN mg/L ORIGINAL SAMPLE, AND WERE CALCULATED AS (CONCENTRATION ON DRY WEIGHT BASIS) X (SS CONCENTRATION IN ORIGINAL SAMPLE) X 10^{-3} $\mu\text{g/L}$ - SS CONCENTRATION IN ORIGINAL SAMPLE IS GIVEN IN TABLE 11.

NOTE: FOR RESULTS REPORTED AS LESS THAN SOME VALUE THE CONCENTRATION IN THE EXTRACT WAS BELOW THE DETECTION LIMIT, HOWEVER COMPOUND WAS STILL PRESENT.

TABLE 16

RESULTS OF SPECIFIC COMPOUND ANALYSES FOR 5:1

NITRIFICATION REACTOR INFLUENT, EFFLUENT AND WASTE ACTIVATED SLUDGE SAMPLES

SAMPLE LOCATION	DATE	SPECIFIC COMPOUND CONCENTRATION IN ORIGINAL SAMPLE (µg/L)					
		ANILINE	BENZOTHAZOLE	2-METHYLMERCA- PTOBENZOTHAZOLE	DIPHENYLAMINE	DIETHYL- PHTHALATE	DIOCTYLPHTHALATE
5:1 TOWN/INDUSTRY FEED (LIQUID FRACTION)	FEB. 27/80 MAR. 4/80 APR. 21/80	<63 1,425 158	<63 75 <63	<63 613 250	<63 <63 <63	198 2,938 <63	63 <13 <63
5:1 TOWN/INDUSTRY FEED (SOLID FRACTION)	FEB. 27/80 MAR. 4/80 APR. 21/80	4 (26) ^b <1 (<7) 23 (217)	3 (18) 3 (19) <2 (<19)	1 (7) 7 (44) 2 (19)	8 (51) 4 (26) 2 (21)	7 (48) 22 (150) 2 (21)	(1,393) (3,525) (195)
5:1 TOWN/INDUSTRY WASTE ACTIVATED SLUDGE COMPOSITE (SOLID FRACTION)	FEB. 27/80 MAR. 4/80 APR. 21/80	<63 <11 <20)*	<28 <11 <20)	(168)* (23) (44)	<28 <11 <20)	(34) (7)* <20)	(539) (207)* (45)
5:1 TOWN/INDUSTRY EFFLUENT (LIQUID FRACTION)	FEB. 27/80 MAR. 4/80 APR. 21/80	<63 <63 <63	<63 <63 <63	88 88 <63	<63 <63 <63	50 13* <63	13 13 <63

^a VALUES NOT IN PARENTHESIS ARE CONCENTRATIONS EXPRESSED IN µg/L ORIGINAL SAMPLE, AND WERE CALCULATED BY (CONCENTRATION ON DRY WEIGHT) X (SS CONCENTRATION IN ORIGINAL SAMPLES) X 10⁻³ µg/L - SS CONCENTRATION IN ORIGINAL SAMPLE IS GIVEN IN TABLE 11.

^b VALUES IN PARENTHESIS ARE CONCENTRATIONS EXPRESSED ON DRY WEIGHT BASIS (mg/kg).

NOTE : FOR RESULTS REPORTED AS LESS THAN SOME VALUE THE CONCENTRATION IN THE EXTRACT WAS BELOW THE DETECTION LIMIT, COMPOUND WAS STILL PRESENT.

at a loading rate of 0.7 grams volatile solids/L-day. Under these conditions, a volatile solids reduction of 68% was achieved with a gas production rate of 0.9 L/g of volatile solids added. All aspects of digester operation were representative of a properly operating system.

6.3 Reproducibility And Recovery Data

In order to evaluate the relative precision (i.e. reproducibility) and accuracy (i.e. recovery) of the extraction and analytical methodologies utilized in this study, some duplicate samples (anaerobic sludge digester samples), and spiked samples (nitrification reactor samples) were analysed by GC/MS. In addition, blank and spiked TOC-free water samples were also analysed. The duplicate sample results are presented in Table 12, the blank and spiked TOC-free water sample results in Table 13, and the spiked nitrified effluent results in Table 14.

The less than sign "<" in Table 12, and in all subsequent Tables implies that the compound was detected. However, its concentration was below the minimum quantification limit of the GC/MS used for the study. In Table 12, when the compound concentration in either one of the two duplicate samples was significantly higher than the GC/MS minimum quantification limit, a percent coefficient of variation "% cv" was calculated. This percent coefficient of variation is not intended for statistical measure, rather it is used to give a relative estimation of the reproducibility attainable with the extraction/analytical methods employed by the study.

Table 12 demonstrates that diphenylamine concentrations in all four sludge samples are at or below the minimum quantification limit, hence its reproducibility could not be estimated. Reproducibility for dioctyl phthalate (% cv $\approx$ 37-66%) was slightly better than those for the other four compounds whose percent coefficient of variation ranged from 83 to 141%. In general, a well operated GC/MS is believed to be capable of reproducing quantitative results within $\pm 10\%$ (Foster, G., 1979). The poor reproducibility experienced in this case can, therefore, be attributed to poor extraction efficiency and other factors discussed in Sections 6.4.1 to 6.4.4.

The "maximum possible" recoveries for the six organic compounds were examined by means of measuring their concentrations in the two spiked TOC-free water samples (see Section 4.3.3 for sample preparation procedures). The data in Table 13 indicate that the "maximum possible" recoveries for benzothiazole, 2-methylmercapto benzothiazole, diphenylamine and diethyl phthalate ($\sim$ 53-65%) were lower than expected. Recoveries for aniline were poorer at 35-41%, while recoveries for dioctyl phthalate (<10-18%) were the poorest. However, recoveries for all six compounds did not appear to be significantly affected by their initial concentrations within the spiked range of 10-50 ng/ μ L per compound.

Percent recovery for the six selected compounds in the sewage samples were determined according to the procedures described previously in Section 4.3.3. Concentrations for the six compounds measured in the original and spiked sewage samples are tabulated in

Table 14, along with their corresponding percent recovery.

According to EPA protocol (EPA, 1979b), recovery in the original and spiked samples can be assumed equal and hence can be calculated by the following formula:

$$\left(\frac{C_s - C_o}{C_i} \right) \times 100\%$$

where C_s , C_o = compound concentrations in the spiked and in the original samples, respectively;

C_i = compound concentration initially spiked into the original sample.

In Table 14, when either one or both concentrations are below the minimum quantification limit (<5 ng/μL), two percent recoveries representing the maximum and the minimum recoveries attained were calculated for the sample stream. The formula for calculating these two recoveries are given in Table 14. In contrast to the percent recoveries observed in Table 13 for the spiked TOC-free water samples, percent recoveries for all six compounds were extremely poor and varied widely from less than zero to greater than 100%. Of the six compounds monitored, percent recoveries for aniline were the most erratic, ranging from -420 to 972%. Maximum variation for the other five compounds were as follows:

benzothiazole	-50 to 475%
2-methylmercapto benzothiazole	-50 to 475%
diphenylamine	-50 to 220%
diethyl phthalate	-50 to 104%
dioctyl phthalate	-127 to 200%

The wide variation in percent recoveries observed in Table 14 can be attributed to poor reproducibility when analysing the complex sewage effluent samples. A greater than 100% recovery in this case would indicate percent recovery is higher in the spiked sample than in the original sample; and conversely a less than zero percent recovery (i.e. negative recovery) indicates that recovery is poorer in the spiked sample than in the original sample.

The reproducibility and recovery problems encountered are not unique to this study. For example, Bridle (1980) reported that EPA has found that it is not uncommon for spiked effluent samples to have recoveries and 3 standard deviation spreads in replicate data to vary from -34 to 500%. It is clear that considerable development and/or improvement on sampling and analytical methodologies are required before reliable quantitative data can be developed in organics monitoring programs. Some of the possible reasons for the deviations encountered in this study are further discussed in the following sections.

6.4 Factors That May Cause Analytical Difficulties

6.4.1 Extraction Procedures

At the outset of the project it was decided to use a broad spectrum solvent, i.e. methylene dichloride, and to do separate acid and neutral base extractions on the samples. In Phase 2, only neutral-base extractions were done. It may be possible to markedly improve the extraction accuracy and reproducibility by using a more specific solvent than methylene dichloride, or a mixture of solvents. For example, recent work performed by the

EPS, Wastewater Technology Centre has indicated that another extraction procedure may be significantly better than methylene chloride for the base/neutral extraction of the solids fraction. The new procedure, still in preliminary stages, involves extraction of the sewage solids with a 1:1 v/v solution of hexane and acetone, followed by ultrasonic agitation, and soxhlet extraction (Lesage, 1980). Organic compounds in coke plant sludge solids were partially separated and tentatively identified using this solvent extraction system, whereas a methylene chloride extract revealed a very high background reading with no discernible component peaks. This promising method is currently being tested with sewage sludge solids.

The U.S. EPA has also encountered problems with recovery of base-neutral compounds using similar extractive methodology. Convery et al (1980) reported that the basic methodology does not capture all the base-neutral compounds which are difficult to chromatograph at low concentrations. A statistical evaluation of data from seven laboratories using the EPA extraction methodology is reported to indicate that recoveries of base-neutral compounds are significantly lower in wastewater (68% recovery) compared to those in distilled water (84% recovery). Moreover, quality control data suggest that percent recoveries of individual organic compounds have ranged from zero to several hundred percent using the EPA methodology, (Convery et al, 1980). These findings suggest that there is considerable room for improvement on extraction methodologies.

In Phase 2, the solid fractions of the samples after sonification, were extracted only once. More recent procedures (Table 1) recommend repeated (up to 3 times) extractions of solid fractions. The lack of repeat extractions in this study may explain some of the variability observed in solid fraction data.

6.4.2 Initial Compound Concentration

Several samples from both the anaerobic digester and nitrification reactors contained organics at, or close to, the GC/MS quantification limit. This factor may have contributed to overall variability. In this regard, McCarty and Reinhard (1980) observed that when the mean concentration of a wastewater compound was less than 5 times the quantification limit for that compound, variance resulting from analysis was less than 50% of the total variance. The effects of detection limit problems could be minimized by extracting a larger volume of the original sample and/or concentrating the extracts to a smaller volume.

Similarly, large variation is also to be expected for compounds occurring at very high concentrations and proper dilution factors have not been applied. In this case, the capillary/packed column in the GC or GC/MS can be easily saturated or poisoned by those compounds and resulting in poor separation.

6.4.3 Volatilization

It is possible that some compounds, specifically aniline, could have been volatilized and lost during the separatory funnel or other extraction procedures employed in this study. The fact that the spiked compound d_5 -nitrobenzene was not identified in any of the samples tends to confirm this factor.

6.4.4 Other Factors

Other factors which may have contributed to the erratic reproducibility and recovery data include:

- (1) sample splitting procedures, i.e. difficult to obtain homogeneous split samples especially for sludge;
- (2) spiking procedures - a "cocktail" of the six compounds was added to each sample prior to extraction. In solid fraction samples, the material may not have been completely mixed by ultrasonification;
- (3) relatively low solvent recovery from some solid fraction samples.

6.5 Trace Organics in the Raw Sewage and Nitrified Effluents

Concentrations of the six selected organic pollutants measured in Phase 2 samples are presented in Tables 15 and 16, for the 2:1 and the 5:1 nitrification reactors, respectively. The performance of the two nitrification reactors was discussed in Section 6.1. The concentrations reported in Tables 15 and 16 were calculated with the assumption that 100% of the organic compound concentration presented in the original sample was recovered. Due to the reproducibility and recovery problems pointed out in previous sections, this assumption is probably invalid. Hence, the organic results obtained in this study cannot be used to perform mass balances around the two bench nitrification reactors as originally intended. To reflect poor reproducibility and recovery efficiency, only those samples which showed one order of magnitude change or greater (i.e. $\geq 1000\%$) after nitrification (marked by an asterisk in the two Tables presented) were used to infer general trends on

the compound removability/accumulation within the nitrification reactors. The compound concentrations measured in the solid phase of the raw sewage samples were reported both on a dry weight basis (mg/Kg) and as microgram present in each liter of the original sample. This latter concentration (mg/L) was used to compare the distribution of the compounds between the liquid/solid phase in raw sewage, and was calculated by means of multiplying the dry weight concentration (mg/Kg), the solids concentration in the original sample presented in Table 11, and a conversion factor of 10^{-3} .

Both Tables 15 and 16 show that in the raw sewage, dioctyl phthalate occurred primarily in the solid phase, while the other five compounds, including phthalate, occurred principally in the liquid phase.

On all three sampling days, aniline, benzothiazole and diphenylamine concentrations in both nitrified effluents (2:1 and 5:1 reactors) were below the GC/MS minimum quantification limit. However, due to fairly low initial concentrations in the raw sewage, change in benzothiazole (except on March 4, in the 2:1 reactor) and in diphenylamine were less than one order of magnitude, hence, no inferences on their removability can be drawn. On the other hand, three of the six analyses performed on the liquid fraction for aniline showed a more than one order of magnitude reduction, and on April 21, in the waste activated sludge sample taken from the 5:1 reactor, aniline also showed a greater than one order of magnitude reduction. It can, therefore, be inferred that in this study aniline was reduced during nitrification even though its removal mechanism was not identified.

On March 4, in the liquid effluent samples collected from both reactors, 2-methymercapto benzothiazole, and diethyl phthalate were reduced by a magnitude either close to or greater than one order. Nonetheless, over these three sampling days, there was insufficient evidence to warrant any inferences on their removability. Since dioctyl phthalate occurred primarily in the solid phase, and it did not appear to leach out to any significant degree in the waste activated sludge solids, hence, with suspended solids reduction occurring in the two reactors in the range of 85 to 95% (see Section 6.1), its removal in the final effluent is expected.

6.6 Aeration Head Space Samples

Tenax organic traps were used during the study to collect air samples being stripped from the two nitrification reactors (see Section 4.1). No detectable levels of organic compounds were detected when the Tenax traps were analysed. This result can probably be attributed to any one or combination of the following three reasons: insufficient volume of gas being passed through the trap; organics not being trapped to any degree by the Tenax; or organics were not eluded to any degree from the Tenax. If concentrations of organics in the aeration head space were low, then the first factor would probably be most significant.

For future organics air sampling of this nature, it will be necessary to develop a more appropriate methodology for sample collection and extraction. Perhaps an air-bag system, such as the one used to collect the digester gas samples (see Section 4.2), would be more appropriate than the organic trap method.

6.7 Occurrence Of The Six Compounds In The Sludge Samples

The six organic compounds were monitored in both the liquid and the solid fractions of the digester feed and effluent samples. Analyses were carried out on duplicate samples. The concentrations in the extract (ng/ μ L) were previously reported in Table 12. These same results are presented again in Table 17 as concentrations found in the original sample (μ g/L or mg/Kg). In converting the results from Table 12 to Table 17, the invalid assumption of 100% recovery was once again used for the calculation.

The lack of agreement between each pair of duplicate sample results is apparent in Table 12 as well as in Table 17. Table 17 shows that aniline, benzothiazole and diphenylamine in all four fractions were present at levels either close to or below the GC/MS minimum quantification limits (i.e. 5 ng/ μ L). The other three compounds occurred at slightly higher levels. Dioctyl phthalate is demonstrated by Table 17 to be strongly hydrophobic while the other five compounds monitored are reasonably hydrophilic.

Due to poor reproducibility and less than one order magnitude change after anaerobic digestion, no inferences on their treatability is drawn in this study.

As pointed out in Section 4.2, the feed to the anaerobic digester was made up of three parts of primary sludge from a pilot scale primary clarifier and one part of waste activated sludge taken from the full scale treatment plant. Consequently, results presented in Table 17 cannot be related to the results obtained from the two bench scale nitrification reactors presented in Tables 15 and 16.

TABLE 17

RESULTS OF SPECIFIC COMPOUND ANALYSES FOR DIGESTER FEED AND EFFLUENT SAMPLES COLLECTED FEB. 4 TO FEB. 8/80

SAMPLE	REPLICATE	ANILINE	SPECIFIC COMPOUND CONCENTRATION (ug/L)					DIETHYL-PHTHALATE	DIOCTYL-PHTHALATE
			BENZOTHIASOLE	2-METHYLMER-CAPTOBENZOTHIASOLE	DIPHENYLAMINE				
DIGESTER FEED (SOLID FRACTION)	REP. NO. 1	(< 4) ¹	(26)	(27)	(< 4)	(34)	(366)		
	REP. NO. 2	(5)	(5)	(< 4)	(4)	(67)	(627)		
DIGESTER FEED (LIQUID FRACTION)	REP. NO. 1	75	< 75	90	< 75	75	15		
	REP. NO. 2	< 69	< 69	847	< 69	7,778	69		
DIGESTER EFFLUENT (SOLID FRACTION)	REP. NO. 1	(< 68)	(< 10)	(< 10)	(< 10)	(21)	(316)		
	REP. NO. 2	(< 10)	(37)	(< 10)	(< 10)	(14)	(115)		
DIGESTER EFFLUENT (LIQUID FRACTION)	REP. NO. 1	< 69	< 69	375	< 69	2,556	56		
	REP. NO. 2	118	< 74	88	74	368	132		

¹ Values in parentheses are concentrations expressed on dry weight basis (mg/kg).

6.8 Digester Gas Sample

The analysis of the biogas sample from the anaerobic digester is summarized in Table 18. Methane content is high at 77.2%, indicative of well-balanced digestion. Hydrogen sulphide was also present in significant quantity (0.01% by volume). A total of nine hydro-carbons or chlorinated hydro-carbons (other than methane) were identified. Compounds in greatest abundance were chiefly aromatic hydro-carbons (e.g. n-propyl benzene, toluene, cumene and mesitylene). Other abundant compounds were cyclohexanone, an aliphatic cyclic ketone and chloroform. None of the six indicator compounds were identified in the digester off-gas indicating that either they were not being volatilized to any significant extent or they were not at high enough concentrations to be detected by the analytical procedures employed.

TABLE 18
COMPOSITION OF BIOGAS FROM BENCH SCALE ANAEROBIC DIGESTER
(3:1 Primary:WAS Feed)

Constituent	Concentration	
Methane	77.2	v/v
Hydrogen Sulphide	1,000	mg/m ³
n-Propyl Benzene ¹	49,870	mg/m ³
Cyclohexanone ¹	27,830	mg/m ³
*Toluene	23,260	mg/m ³
Cumene ¹	6,906	mg/m ³
*Chloroform	4,091	mg/m ³
Mesitylene ¹	1,175	mg/m ³
Carbon Disulphide	783	mg/m ³
*Trichloroethylene	97.5	mg/m ³
*Tetrachloroethylene	78.4	mg/m ³
Propane	61.8	mg/m ³

¹ Tentatively identified by gas chromatography

* EPA Priority Pollutants

7.0 Comparative Data

A review of the literature on organics in wastewaters is presented in Section 2. Wherever possible, quantitative data were extracted from published reference material and summarized in Table 19. It should be noted that several studies involving organics monitoring are ongoing for which very little data is published (e.g. EPA 40 POTW program).

No data could be found on the occurrence of 2-methylmercapto benzothiazole. Diethyl- and dioctyl phthalate are the two most frequently found compounds in sewage influent, effluent and sludges. As indicated in Appendix B, dioctyl phthalate has a high bio-accumulation factor (up to 100,000 times in certain organisms). In addition, phthalates are also being listed as persistent toxic substances in the Great Lakes Water Quality Agreement (IJC, 1978). Dioctyl phthalate is in the Michigan DNR Critical Material Registry (CMR) and is listed as one of the EPA's priority pollutants. The MOE "Blue Book" (1978) specifies a water guideline of 0.2 µg/L or less for phthalate esters.

A comparison of the observed off-gas concentration to US occupational and MOE ambient air guidelines is made in Table 20. Most of the gases measured are of low toxicity with the exception of methane, hydrogen sulphide and toluene.

TABLE 19
SUMMARY OF EXISTING QUANTITATIVE DATA FOR
SUBJECT COMPOUNDS IN WASTEWATERS

Wastewater Type	Diethyl Phthalate	Di-n-octyl Phthalate	Diphenylamine	Benzothiazole	Aniline	Reference
Primary Effluent	0.4 µg/L	-	-	-	-	Mori et al (1978)
Influent	0-6 µg/L	not detected	-	-	-	Feiler (1979)
Secondary Effluent	0-3 µg/L	0-1 µg/L	-	-	-	
Sludges	not detected	not detected	-	-	-	
Tire Mfg. Waste	60 µg/L	-	200 µg/L	20-60 µg/L	-	Jungclaus et al (1976)
Specialty Chemicals Waste	-	not detected	-	not detected	20 µg/L	Jungclaus et al (1978)
SynFuel Wastewater	-	-	-	-	5 mg/L	Lamb et al (1979)
Influent, Three Municipal Treatment Plants	Total Phthalates 9-90 µg/L		-	-	-	Ongerth and De Walle (1980)
Influent Seattle	6.6 µg/L	5.6 µg/L				
Sec. Effluent Seattle	0.2 µg/L	1.8 µg/L				
Sludge Seattle	6.0 µg/L	120 µg/L				
Influent Oakland	9.8 µg/L	11. µg/L				Convery (1980)
Sec. Effluent Oakland		6 µg/L				
Sludge Oakland		1.8 µg/L				
Influent Atlanta	1.4 µg/L	13 µg/L				
Sec. Effluent Atlanta	0.3 µg/L	5 µg/L				
Sludge Atlanta		200 µg/L				
Influent Water Factory 21 Orange County	2.5 - 13 µg/L	1.7 - 14 µg/L				Reinhard et al (1979)
Effluent Water Factory 21	0 - 6.0 µg/L	0.4 - 6.0 µg/L				
Industrial Effluents (General)	Total Phthalates 55-2000 µg/L		-	-	1.2 - 16.5 µg/L	Waggott and Wheatland (1977)

In spite of a number of organic priority pollutants measured in the digester off-gas, the off-gas was not felt to be of environmental concern. Firstly, nobody works in the digester when the digester is operating. Secondly, in any full-scale digester installation the off-gas would be burned as a fuel or as an off-gas flare at high temperature ($\sim 1200-3400^{\circ}\text{F}$) (Perry, 1973) before being released to the environment. This burning would significantly reduce the levels of most of the observed compounds.

TABLE 20

COMPARISON OF DIGESTER GAS COMPOUNDS TO
U.S. OCCUPATIONAL AND MOE ENVIRONMENTAL LEVELS

Compound	Off Gas Concentration (This Study) $\mu\text{g}/\text{m}^3$	U.S. Occupational Levels		MOE Environmental Levels	
		$\mu\text{g}/\text{m}^3$	<u>Conc</u>	Env. Conc $\mu\text{g}/\text{m}^3$	<u>Conc</u>
			$\div$ TWA		$\div$ Env. Conc
Methane	5.1×10^8	-	-	-	-
Propane	61.8	1.8×10^6	3×10^{-5}	-	-
Hydrogen Sulphide	1×10^6	15000	67	30	3.3×10^4
Carbon Disulphide	783	6.0×10^4	0.01	330	2.4
Toluene	23258	3.75×10^5	0.06	2000	11.6
Trichloro-ethylene	97.5	5.35×10^5	2×10^{-4}	8.5×10^5	1×10^4
Tetrachloro-ethylene	78.4	6.70×10^5	2×10^{-4}	-	-
Chloroform	4091	5.0×10^4	0.08	1500	2.7
Xylene	6906	2.45×10^5	0.03	100	69
Cyclohexanone	27832	2.0×10^5	0.14	-	-
n-propyl benzene	49870				
mesitylene	1175				

TWA = Time Weighted Average

(the TWA concentration for a normal 8 hr. work day or 40 hour work week, to which nearly all workers may be repeatedly exposed day after day without adverse effect)

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APPENDIX A

Extraction Techniques

Liquid/Liquid Extraction

This method is rapid and has acceptable recovery for many organic compounds of interest in the environment including 80 of the compounds defined as unambiguous priority pollutants by EPA.

Apparatus

Separatory funnels - 1 liter with teflon stopcock

Flask for rotary evaporation

Graduated conical centrifuge tubes

Procedure

Wash thoroughly all glassware to be used in the extraction procedure with the solvent to be used. Transfer 800 ml of sample into the separatory funnel.

Base/Neutral Extraction

Adjust the pH of the sample to 11 or greater using 6N NaOH. Use multi range pH paper for the measurement. Serially extracted with 80 x 30 x 30 ml portions of distilled-in-glass methylene chloride (soluble to the extent of 2% in water and not recoverable). Each extract must be shaken vigorously for at least 2 minutes by the clock. The phases are allowed to settle for 3 minutes or until the two phases are distinct. The solvent is then filtered through pre-washed glass wool and pre-extracted granular sodium

sulphate. The combined extracts are then rotary evaporated to near dryness using water pressure to create a vacuum and a water bath at room temperature $\pm 5^{\circ}\text{C}$.

The concentrated extract is then transferred to a calibrated tube. The sample is rinsed into the tube with the same solvent using 2 ml, 1 ml and 1 ml aliquots. The same pipette used for transferring the liquid is then used for the final evaporation step so that cross-contamination is avoided. The tube is placed in a water bath with a flow of nitrogen which is barely perceptible in order to reduce the incidence of aerosols. The pipette is lowered as the solvent evaporates. Evaporation is continued until the appropriate volume of solvent remains, the volume is then made up to 1.5 ml with methylene chloride. The tube is then capped with a teflon-lined cap and stored in the refrigerator until the analysis is performed.

Acid Extraction

Adjust the pH of the base-neutral extracted water with 1:1 v/v H_2SO_4 to 2 or less. Serially extract with 40 x 20 x 20 ml portions of distilled-in-glass methylene chloride. Proceed as described for the base-neutral extract.

Blanks

An extraction of millipore-water should be carried out with each set of samples analyzed to act as a blank. The amount of solvent used in each step should be identical to that used for the samples.

Emulsions

Various techniques can be used in order to break emulsions.

These include:

- (1) Addition of pre-extracted sodium chloride.
- (2) Addition of excess solvent.
- (3) Draw off the small amount of free solvent that separates and slowly drip it back in the top of the separatory funnel through the sample and emulsion.

Other possibilities if these fail: centrifugation, passing emulsion through methylene chloride - wet glass wool, allowing to stand for up to 24 hours, stirring with glass rod, heating on a steam bath, sonification.

All these techniques which involve any additions to the sample should also be applied to the blank.

Evaporation

Rotary evaporation cautions:

- (1) If the water bath temperature is too high, bumping can occur and this can cause loss of sample.
- (2) Never allow flask to go to dryness.

Extraction

If analyzing at ppt level, blanks should be run on all glassware prior to use.

If benzene is used as an extraction solvent, equal volumes of solvent are used in the three stages (e.g. for PAH analysis, extraction of 1 L water with benzene use 50 x 50 x 50 ml; with methylene chloride 100 x 25 x 25 ml).

Soxhlet Extraction

This procedure is applicable to samples which require a longer period for complete extraction of organics (e.g. from complex biological or soil matrices).

Apparatus

Glass soxhlet extractor

Extraction Thimble - pre-washed by placing into apparatus with solvent and allowing at least 10 rinses before discarding solvent and using thimble.

Heating mantle

Materials

Distilled in glass solvent-benzene, methylene chloride

Pre-extracted glass wool

Bumping chips

Procedure

Place material to be analyzed in the extraction thimble in the apparatus. The amount of material used will depend on the origin and the type of sample. As a general guideline, 10 g of fish, 20 g of soil or sediment can be extracted. Solvent is placed in a round-bottomed flask in a heating mantle. For 10 or 20 g of material, 200 ml of solvent should be used. The solvent is allowed to boil gently and the extraction is carried out for 16 hours. The organics are then concentrated by the techniques used for liquid/liquid extraction.

Notes

- (1) The technique may be scaled up or down by using the appropriate size of apparatus with a suitable thimble and quantity of solvent.
- (2) Methylene chloride may be used as the solvent or cyclohexane (for PAH analysis).

Solid/Liquid Extraction

This technique can be applied in a situation where a rapid extraction is required and quantitation is not important. Spiking a complex matrix with an internal standard may not give a good indication of the recovery of various classes of compounds from the matrix.

APPENDIX B

Properties, Use and Environmental Hazards of the Six Organic Compounds Monitored During Phase 2

- i) Diphenylamine
- ii) Dioctyl Phthalate
- iii) Diethyl Phthalate
- iv) Methylmercaptobenzothiazole
- v) Benzothiazole
- vi) Aniline

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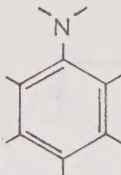
Compound: Aniline

Formula: C_6H_7N

Molecular Weight: 93.13

Synonyms: Phenylamine, Aminobenzene, Aminophen, Kyanol

Structure:



Physical Properties:

- Appearance: Oily liquid, colourless when freshly distilled. Characteristic odour.
- Melting Point: -6.2°C
- Boiling Point: 184.3°C @ 760 mm, 69.2°C @ 10 mm
- Density: 1.0216^{20}
- Refractive Index: 1.5863_D^{20}
- Vapour Pressure: 1 mm @ 35°C , 0.3 mm @ 20°C
- Vapour Density: 3.22
- Solubility: 1 g/28.6 mL H_2O ; miscible with benzene, chloroform, alcohol and most other organic solvents.

Toxicity: Human: Serious poisoning may result from ingestion of 0.25 ml. Acute - cyanosis, methemoglobinemia, vertigo, headache, mental confusion. Chronic - anemia, anorexia, weight loss, cutaneous lesions. Dogs: $\text{LD}_{50} = 500 \text{ mg/kg}$ orally.

Toxic Hazard Rating: Acute Local: Allergenic 2.
Acute Systemic: Ingestion 3; Inhalation 3; Skin Absorption 3.
Chronic Local: Allergenic 2.
Chronic Systemic: Ingestion 3.
Inhalation 3; Skin Absorption 3.

Environmental Concerns: 75% inhibition of nitrification at 7.7 mg/L.
Bacteria: E. Coli: no inhibition @ 1 g/L.
Pseudomonas Putida: inhibition of cell multiplication @ 130 mg/L.
Algae : Scenedesmus: toxic @ 10 mg/L.
Microcystis Aeruginosa: inhibition of cell multiplication starts @ 0.16 mg/L.
Arthropoda: Daphnia: toxic @ 0.4 mg/L.

Use: Manufacture of dyes, medicinals, resins, varnishes, perfumes, shoe blacks, vulcanizing rubber and as a solvent.

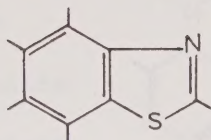
Compound: Benzothiazole

Formula: C_7H_5NS

Molecular Weight: 135.19

Synonyms:

Structure:



Physical Properties:

- Appearance: Yellow liquid with unpleasant odour of quinoline.
- Melting Point:
- Boiling Point: 231°C @ 760 mm, 131°C @ 31 mm
- Density: 1.2384^{22}_4 , 1.246^{20}_4
- Refractive Index: 1.6379^{20}_D , 1.6039^{22}_D
- Vapour Pressure:
- Vapour Density:
- Solubility: Slightly in water, freely in alcohol, ether, carbon disulphide.

Toxicity: Human: Not available.

Mice: LD_{50} = 100 mg/kg intravenously.

Toxic Hazard Rating:

Acute Local:	Unknown
Acute Systematic:	Unknown
Chronic Local:	Unknown
Chronic Systematic:	Unknown

Environmental Concerns:

Odour problems in water at low concentrations. Threshold odour concentrations at room temperature = 0.08 ppm.

20% of population still able to detect odour at 1.8 ppb.

10% of population still able to detect odour at 0.26 ppb.

1% of population still able to detect odour at 0.41 ppt.

Use: Rubber chemicals manufacture and photographic dyes manufacture.

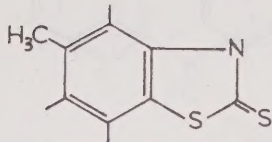
Compound: Methylmercaptobenzothiazole

Formula: $C_8H_7NS_2$

Molecular Weight: 181.28

Synonyms:

Structure:



Physical Properties: - Appearance:

- Melting Point: 171^o-186^oC depending on isomer

- Boiling Point:

- Density:

- Refractive Index:

- Vapour Pressure:

- Vapour Density:

- Solubility: 4 methyl isomer soluble in hot

acetic acid. 5 methyl isomer soluble in hot

toluene. 6 methyl isomer insoluble in

water, soluble in alcohol, acetone hot benzene.

Toxicity: Information not available.

Toxic Hazard Rating: Acute Local:

Acute Systemic:

Chronic Local:

Chronic Systemic:

Environmental Concerns: Information not available.

Use: Information not available.

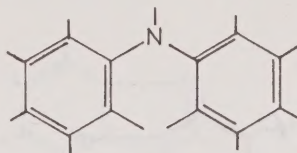
Compound: Diphenylamine

Formula: $C_{12}H_{11}N$

Molecular Weight: 169.22

Synonyms: N-phenylaniline, Anilobenzene, DPA

Structure:



Physical Properties: - Appearance: Monoclinic and Leaf Crystals.
Floral Odour.

- Melting Point: 52.8°C
- Boiling Point: 302°C @ 760 mm, 179°C @ 22mm
- Density: 1.160_{20}^{20}
- Refractive Index -
- Vapour Pressure: 1 mm @ 108.3°C
- Vapour Density: 5.82
- Solubility: Insoluble in water; soluble in ether, benzene, acetic acid, ligroin; very soluble in alcohol and pyridine.

Toxicity: Human - may be irritating to mucous membranes.
- methemoglobinemia has been induced experimentally.
- symptoms are similar to aniline, but DPA is less toxic.

Toxic Hazard Rating:	Acute Local:	U
	Acute Systemic:	Ingestion 3; Inhalation 3; Skin Absorption 3.
	Chronic Local:	U
	Chronic Systemic:	Ingestion 3; Inhalation 3; Skin Absorption 3.

Environmental Concerns: A recognized carcinogen.

Use: Manufacture of dyes, stabilizing nitrocellulose explosives and celluloid; in analytical chemistry for detection of nitrate, chlorate and other oxidizing substances; in veterinary medicine, as one of active ingredients in topical agents for prevention and treatment of screw worm infestation.

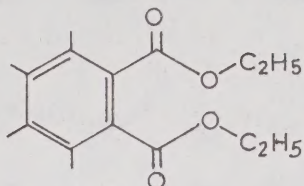
Compound: Diethyl Phthalate

Formula: $C_{12}H_{14}O_4$

Molecular Weight: 222.23

Synonyms: Ethyl Phthalate, DEP

Structure:



Physical Properties:

- Appearance: Colourless, practically odourless, oily liquid.
- Melting Point: $-40.5^{\circ}C$
- Boiling Point: $295-6^{\circ}C$
- Density: 1.232^{14}_4 , 1.120^{25}_{25}
- Refractive Index: 1.5049^{14}_D
- Vapour Pressure: 14 mm @ $163^{\circ}C$, 30 mm @ $182^{\circ}C$, 734 mm @ $295^{\circ}C$
- Vapour Density: 7.66
- Solubility: Insoluble in water; soluble in benzene; miscible with alcohol, ether and many other organic solvents.

Toxicity: Rabbit: $LD_{50} = 1.0$ g/kg orally.

Human: Irritating to mucous membranes, and, in high concentrations, narcotic.

Toxic Hazard Rating: Acute Local: Irritant 2; Ingestion 2; Inhalation 2.

Acute Systemic: Inhalation 2

Chronic Local: U

Chronic Systemic: U

Environmental Concerns: Bacteria: *Pseudomonas putida* - inhibition of cell multiplication starts at 400 mg/L.
Algae: *Microcystis aeruginosa* - inhibition of cell multiplication starts at 15 mg/L.

Use: Manufacture of plasticizers and plastics; rocket propellant and explosive; food packaging applications; dye application agent; diluent in polysulfide dental impressions materials solvent; wetting agent; substitute for camphor in celluloid manufacture; fixative for perfumes; alcohol denaturant; component in insecticidal sprays and mosquito repellants; solvent for cellulose acetate in manufacturing of varnishes and dopes.

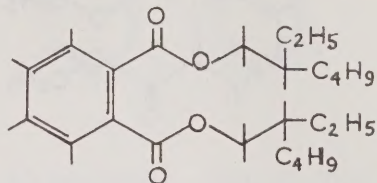
Compound: Dioctyl Phthalate

Formula: $C_{24}H_{38}O_4$

Molecular Weight: 390.54

Synonyms: Di-sec-octyl Phthalate, Bis (2-ethylhexyl) Phthalate,
Di (2-ethylhexyl) Phthalate, Octoil, DOP

Structure:



Physical Properties:

- Appearance: Light coloured liquid; mild odour.
- Melting Point: -55°C
- Boiling Point: 385°C ; 230°C @ 5 mm.
- Density: 0.99^{20}_{20}
- Refractive Index:
- Vapour Pressure: 1.2 mm @ 200°C
- Vapour Density: 13.45 - 16.0
- Solubility: Insoluble in water

Toxicity: Human: No specific data.
Rat : Teratogenic

Toxic Hazard Rating: Acute Local: Irritant 0; Allergen 0;
Ingestion 1; Inhalation 1.
Acute Systemic: Inhalation 2.
Chronic Local: Irritant 0; Allergen 0.
Chronic Systemic: Ingestion 2;
Inhalation 2; Skin Absorption 1.

Environmental Concerns: In U.S., maximum allowable concentration in Class I water (potable water production) is 2.8 mg/L.
Bioaccumulation after 33 d in model eco-system (water concentration = 0.00034 ppm)

Species	Concentration in Species	Bioaccumulation Factor
Algae: Oedogonium	18.32 ppm	53,890x
Mollosca: Physa	7.30 ppm	21,480x
Insect: Culex Pipiens Quienque- faseiatus	36.61 ppm	107,670x
Fish: Gambusia Affinis	0.044 ppm	130x

Use: Manufacture of plasticizers and plastics, recycling, organic pump fluid.

CA20NEV 82E82

Ontario. MOE.

Research Report No.82

MONITORING OF SELECTED TRACE ORGANICS DURING BIOLOGICAL
WASTEWATER TREATMENT. 1982.

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